A LABORATORY STUDY OF THE ADHESION OF A RESTORATIVE ACRYLIC RESIN AND A POLYCARBOXYLATE CEMENT ON BOVINE ENAMEL ETCHED WITH FIFTY PER CENT PHOSPHORIC ACID

by

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....."While the expanding fields of knowledge in the physical and biological sciences have had a profound effect on all areas of dental theory and practice, none have been influenced more than the science of dental materials."

Ralph W. Phillips
(New York State Dental Journal, 1962)

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TABLE OF CONTENTS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

Dentistry has long awaited the development of a truly adhesive dental material capable of providing permanent adhesion to tooth structure under oral conditions.[1] Such an ideal material would radically change the practice of dentistry. In operative dentistry, cavity design could be modified to permit the removal of minimal amounts of tooth structure, since retention and resistance form would be less important. Fractured anterior teeth could be restored without the use of pins for retention.[2,3] In orthodontics, brackets and wires could be luted directly to the tooth surface without the use of bands.[4-10] Susceptible pits and fissures of newly erupted teeth could be sealed and protected against caries.[11-15] According to Phillips,[16] "the rationale behind the selection and use of cavity varnishes and liners would be different with an adhesive material because marginal leakage could be prevented."

An adhesive restorative material capable of adhering to tooth structure under oral conditions would be expected to seal against the ingress of oral fluids, debris, and bacteria.[17,18,19] For adhesion to exist, the surface of the adherend and adhesive must be in close adaptation to

each other, in the order of two angstroms. Numerous studies have shown that all restorative materials exhibit varying degrees of marginal leakage,[20-35] and that no material in current use can provide a permanent adhesive bond on untreated tooth structure under clinical conditions.[32,36-42]

Recently, there has been substantial progress in the research and development of an adhesive dental material.[6-10, 14,15,43-50] However, since an adhesive dental material is not commercially available at present, other methods of enhancing the adhesion of present dental materials to tooth structure should be considered.

The literature contains reports that surface treatment of tooth structure with inorganic or organic acids will increase the adhesion of restorative dental resins.[3,8, 9,12,14,38,42,51-60]

Doyle[2] has advocated restoring small incisal fractures with restorative acrylic resin without the use of pins for retention. The mechanical retention of the resin is supposedly achieved by etching the enamel surface with 50 per cent phosphoric acid before applying the resin.

The main purpose of the present laboratory investigation was to determine whether there is an increase in the adhesion of a conventional unfilled restorative resin to enamel

surfaces etched with phosphoric acid. In order to do this, flat bovine enamel surfaces were etched with a 50 per cent aqueous solution of phosphoric acid for 60 seconds before the resin material was applied. A limited number of resin restorations were also placed in phosphoric acid-etched cavity preparations in extracted human teeth and radioactive calcium (Ca^{45}) was used to assess the marginal seal. The adhesion of a new polycarboxylate cement was also tested on acid-etched enamel surfaces.

REVIEW OF THE LITERATURE

For purposes of organization and clarity, the review of the literature will be separated into three sections: I - Principles of Adhesion; II - Maintaining Adhesion in the Oral Cavity; and III - Methods to Increase Adhesion.

I - Principles of Adhesion

Adhesion is defined as "the force which causes two substances to attach when they are brought into intimate contact with each other."[61] Surfaces which are flat at the molecular level will adhere spontaneously to each other as long as a very close relationship is maintained.[62] Consequently, "the nature of adhesion between two surfaces is dependent upon forces of molecular attraction of no more than one or two ten-thousandth of a micron."[17]

The adhesive is the material or film used to produce the adhesion and the adherend is the material to which the adhesive is applied.[61]

The principle of adhesion is dependent upon the surface energy of the adherend, the wetting characteristic of both the adherend and adhesive, and the contact angle formed between the adhesive and adherend.[9]

The energy beneath the surface layer of a solid material is said to be small because the atoms are mutually and equally attracted. However, the energy at the surface

layer is greater because the atoms on the surface are not equally attracted and have a stronger attraction for each other. Therefore, the greater the surface energy, the greater the attraction for unlike molecules, and hence the greater the capacity for adhesion.[9,61]

Theoretically, surfaces which are absolutely flat should adhere to each other. However, for all practical purposes surfaces are far from being smooth or flat, so that it becomes necessary for the adhesive to flow and spread easily over the entire surface of the adherend in order to achieve molecular closeness.[62] This characteristic is referred to as "wetting."[61] Adhesion is therefore dependent upon the ability of the adhesive to wet the surface of the adherend. If the adhesive is unable to wet the surface of the adherend because of low surface energy or the presence of debris or water, adhesion will be difficult to achieve and maintain.

Rose[63] found that materials which "wet" the surface easily and quickly exhibited somewhat better adhesive characteristics.

The ability of an adhesive to wet the surface of the adherend can be determined by measuring the contact angle between the adhesive and adherend.[61] As the ability of an adhesive to wet the surface of the adherend increases, the contact angle decreases. A liquid that is able to form a

small contact angle is said to have better wetting and adhesion properties than one that forms a large contact angle on the same surface.[64]

Ideally, then, to obtain and maintain adhesion, the adhesive and adherend should possess the following properties.

Adherend

1. High surface energy to provide greater attraction for unlike molecules.
2. Homogeneous and smooth surface.
3. Absence of surface moisture.
4. Surface clean and free of debris, so wetting can take place.

Adhesive

1. Low energy to permit wetting of the adherend.
2. Displaces or makes use of water, so wetting can take place.

II - Maintaining Adhesion in the Oral Cavity

Many investigators have recognized that maintaining adhesion of restorative dental materials to tooth structure is difficult because of conditions within the oral environment,[4,6,9,18] the heterogeneous composition and surface irregularities of enamel and dentin,[4,9,16,18,48,65] and the failure of current restorative materials to provide a leakproof seal and permanent adhesion to tooth structure.[20-42, 66-69]

Conditions in the oral cavity

Phillips[18] has stated that "forces of mastication, instantaneous temperature changes, rapidly fluctuating pH, and the warm humid environment of the oral cavity make adhesion of restorative materials to tooth structure difficult and unsuitable."

The presence of moisture within the oral environment appears to interfere with adhesion of dental materials because of molecular fluid migration between the adhesive and adherend.[6,17,70] Christie[71] conducted adhesion tests against glass, polished steel, wet and dry bone, and human tooth structure. He found that moisture eventually destroyed the adhesion of direct acrylic resins to the various surfaces. In evaluating the adhesion of dental cements and restorative acrylic resins, Swartz and Phillips[37] noted that adhesion was greatly reduced when the specimens were immersed in water. A monolayer of water present upon the hydroxyapatite crystal of enamel and dentin further complicates the problem of maintaining adhesion.[4,9,61,65,70]

Lee[48] has stated that teeth or bone are rather poor substrates when one attempts to adopt the industrial approach in developing biological adhesives for hard tissues. One of the problems with hard tissue is its hydrophilic nature. "Since water has a higher energy of adsorption, it tends to displace absorbed adhesive polymer molecules, making lasting adhesion difficult."

Tooth structure and its surface

The composition of human enamel and dentin is heterogeneous, being partly inorganic and partly organic.[9,61] Phillips[16,18] has stated, "An adhesive which would adhere to the organic component may not adhere to the inorganic component of enamel or dentin."

Enamel and dentin surfaces have been described as irregular and porous, exhibiting many surface imperfections as well as containing microscopic debris.[4,9] Surface roughness and debris produced during cavity instrumentation prevent proper wetting of an adhesive material.[9,18,73,74]

According to Phillips,[16] "Surface irregularities may act as areas of stress concentrations upon application of mechanical and thermal stress which could eventually break the adhesive bond of the adhesive from the adherend."

Restorative dental materials

A survey of the dental literature reveals that all restorative and luting materials exhibit varying degrees of marginal leakage.[20-35] The author will not attempt to review all of the many studies concerning marginal leakage of restorative materials. Only selected studies evaluating restorative dental resins and cements will be reviewed since these two materials were used in this investigation.

In 1952 Nelson, Wolcott, and Paffenbarger[22] placed a number of restorative materials in extracted teeth and

immersed them into ice water. Accumulation of moisture was observed under a microscope at the margins of the resin restorations when the teeth were warmed with the fingers. The authors called this phenomenon "marginal percolation." They concluded that it resulted in part from the difference in the thermal coefficient of expansion of tooth and resin and the thermal expansion of the fluid occupying the crevice between tooth and restoration.

Sausen and Armstrong[20] in 1952 measured the marginal adaptation of acrylic resins placed in sound extracted teeth by observing the penetration of Ca^{45} radioisotope. The autoradiographs revealed that Ca^{45} penetrated every margin, with the least penetration observed around resin restorations inserted by the non-compression technique.

In 1955 Seltzer[25] used two microorganisms which revealed themselves by a characteristic color production to assess the sealing quality of restorative acrylic resins. He discovered that when the resin restorations underwent thermal changes, many of them permitted the passage of the microorganisms. In no instance did the organisms penetrate the margins of restorations not subjected to thermal changes.

Hirsch and Weinreb[26] in 1958 used capillary diffusion of dyes to investigate the cavity sealing properties of direct filling resin, silicate, and zinc phosphate cement.

They observed dye penetration around the margins of all materials when the teeth were immersed in a cold dye solution ($4^{o}C$) and a hot dye solution ($60^{o}C$).

Using I^{131} radioisotope, Going et al[27] in 1960 compared the marginal seal of restorative materials commonly used. Laboratory data revealed that all filling materials exhibited some marginal penetration of the radioisotope, with acrylic resins demonstrating the most marginal leakage.

Swartz and Phillips in 1961[28] reported the effect of thermal change on the marginal leakage of a limited number of direct restorative resins. Specimens were placed in warm and cold solutions of Ca^{45} isotope at five-minute intervals. The effects of $10^{o}C$, $20^{o}C$, and $40^{o}C$ temperature differentials were studied. Contrary to other studies,[30,31] they did not observe a marked increase in the marginal leakage of resin restorations subjected to the varied temperature changes. Silicate and zinc phosphate cements exhibited penetration of the isotope in varying amounts.

The marginal adaptation of restorations placed in the teeth of dogs and human beings was reported by Phillips et al.[29] Using Ca^{45} to assess the marginal seal of the restorative materials, they observed that restorative acrylic resins displayed some degree of marginal leakage of radioisotope in both the extracted teeth of dogs and

human beings. Some leakage was observed with the zinc phosphate cement restorations; however, there appeared to be less penetration with older restorations.

In one part of a comparative laboratory study of the physical properties of several selected self-curing resin filling materials, Peterson,[69] in 1966 investigated the effect of temperature stress cycling and storage in water on the marginal seal of the dental resin materials. Autoradiographs revealed that Sevriton resin demonstrated little or no Ca^{45} isotope penetration even after three-month storage. Specimens that were temperature cycled between 15°C and 45°C revealed leakage patterns similar to those of specimens held at constant temperatures. However, a substantial increase in isotope penetration was observed in all of the resin restorations when they were subjected to a 60°C temperature differential.

Instead of radioisotopes, Christen[33] used fluorescent dyes to assess the marginal leakage of restorative dental materials placed in bovine teeth. Zinc phosphate cement restorations demonstrated leakage to the pulp within five minutes when immersed in a two per cent fluorescein solution. When immersed in rhodamine B, leakage reached the pulp within one hour. The investigator's criterion for measuring marginal leakage is not necessarily indicative of the relative ability of the materials to seal the cavity; it may be more indicative of the dentin's permeability to the dye.

Other investigators[21,26,31] have reported that the high thermal coefficient of expansion of conventional restorative resins is the reason for the increased marginal leakage observed with these materials.

However, Guzman[35] in 1968 reported that after thermal cycling both a conventional restorative resin and a composite resin, the conventional resin exhibited better marginal seal. This was despite the fact that the new resin had a much lower thermal coefficient of expansion than did the older materials.

It may be surmised that the marginal leakage of restorative dental materials is the result of the loss or lack of adhesion between filling material and tooth structure. Buonocore[38,51] has stated that "one of the major shortcomings of restorative acrylic resins is their lack of true adhesion to tooth structure."

In evaluating a method for increasing the adhesiveness of dental cements, Swartz and Phillips[37] reported that restorative acrylic resins possessed better adhesive properties on dry dentin surfaces than zinc phosphate cement, but this adhesion was greatly reduced when subjected to water immersion.

Johnson et al[67] in 1955 evaluated the effectiveness of resin cements as luting agents for single and multiple crown and bridge restorations after 28 months of service

under oral conditions. It was observed that resin cements exhibited greater "adhesive" characteristics than the zinc phosphate cements. However, the increased adhesion observed with the resin cements was probably related more to mechanical retention than to the "adhesive" characteristic of the material per se.

In 1956 Schouboe and Paffenbarger[39] tested the adhesion of various resin materials applied to the flat surfaces of extracted teeth. They reported that all of the materials exhibited initial adhesion on hard tooth structure. However, after 24 hours immersion in water, most of the resin cements became dislodged, and after one week all of the resin cements became dislodged.

Griffith[40] in 1960 concluded that zinc phosphate cement owed only a small percentage of its retention to adhesion.

Mahler and Armen[68] also studied the adhesion of zinc phosphate cement with and without the addition of amalgam particles. No adhesion was observed with either the regular or amalgam-added cements stored in water and in 100 per cent humidity.

Using extracted human maxillary central incisors and reinforced orthodontic bands, Williams[36] in 1963 measured the retentive ability of various cementing agents with a mechanical testing device. Results showed that zinc

phosphate cement was capable of providing relatively strong bonds to natural teeth. The mean retentive value was 540 psi. Silicophosphate cements exhibited retention values almost identical to those of the zinc phosphate samples. Storage in water reduced the retentive values for all of the cements tested.

Peterson[69] concluded from his study that clinical retention of any of the direct filling resin systems should not be based upon an "adhesive" property of the material per se, but only upon mechanical retention. Sevriton resin demonstrated initial resistance to separation under a tensile load. However, this resistance decreased after one-week storage in water.

Smith and Williams[41] reported similar findings. By their test, acrylic resin filling materials exhibited little or no adhesion when subjected to a tensile load. Hanke[42] also reported that Sevriton acrylic resin demonstrated relatively little adhesive quality on polished dentin surfaces when subjected to a tensile load.

The high thermal coefficient of expansion and the 6 to 8 per cent volumetric shrinkage[75] are two physical properties of restorative acrylic resin systems that have been said to decrease their adhesion to tooth structure and increase the possibility of marginal leakage.[16,76]

Bowen[118] hypothesized that "for a dental restoration to fill a cavity and retain close adaptation to the cavity walls, the adhesion or bond strength between the filling material and the tooth structure at all times must be as great as the tensile and shearing stress tending to separate the material. The disruptive forces may arise in part from the high coefficient of thermal expansion and volumetric shrinkage."

Using five different methods for measuring the tensile forces during the setting of commercial resins, silicates, and zinc oxide eugenol cement, Bowen discovered that tensile stresses developed in self-curing sulfinic acid resins during polymerization, if large enough, could result in the displacement of the filling material from the cavity walls.[118]

The non-pressure bead method of inserting conventional sulfinic acid resin systems has been shown to compensate for the 6 to 8 per cent volumetric shrinkage,[70-80] and also provide a more effective seal than the pressure bulk pack method.[23,24,81,82]

Even with the introduction of the newer composite resin systems, which have a lower thermal coefficient of expansion and volumetric shrinkage, the problem of marginal leakage is still present.[19,32,35]

It has been stated that the modulus of elasticity represents an index of the stiffness and resistance of a restorative material to forces which may cause marginal displacement.[83] Hence, this physical property may influence the marginal adaptation of dental materials to the cavity walls of a preparation. A material with a low modulus of elasticity could conceivably bend or break away from the cavity margins under occlusal forces.

The modulus of elasticity of acrylic resin is much lower than that of enamel and dentin.[83-86] This means that if an acrylic resin restoration is not supported by surrounding tooth structure, marginal deformation can occur.

Zinc phosphate cement is routinely used for luting fixed cast restorations or orthodontic bands to teeth. According to Skinner and Phillips,[61] the luting ability of zinc phosphate cement is purely mechanical and does not form a true adhesive joint. Mechanical retention is achieved by the interlocking of the finger-like extensions of cement between the surface irregularities of the tooth surface and the material to be luted. The degree of mechanical retention is influenced in part by the inherent physical properties of the cement.

Zinc phosphate cement dissolves and disintegrates in the oral fluids.[87] The American Dental Association Specification No. 8 specifies that zinc phosphate cement

must not exceed a maximum solubility of 0.30 per cent by weight during immersion in distilled water for seven days.[88] However, solubility studies in dilute organic acids indicate that zinc phosphate cements are more soluble in acids than in distilled water.[89,90] Also when the pH of the solution is decreased, dissolution of the cement is higher.[89,90] This undesirable property makes it almost impossible to lute orthodontic brackets to teeth in the oral cavity for indefinite periods without the use of bands.

The compressive, tensile, and shear strength of the cement may influence its retentive ability. The stronger the cement, the less likely it is that the finger-like extensions of cement will fracture, and hence, the greater will be the capacity for mechanical retention.[61]

III - Methods to Increase Adhesion

It is apparent from the review of the literature that none of the commercial dental materials can maintain permanent adhesion to tooth structure under oral conditions. This has prompted researchers to consider the following approaches to this complex problem:

(1) the development of a new adhesive material for dental use;

(2) the development and use of an adhesive liner between the filling materials and tooth structure, and

(3) the treatment of the tooth surface with either surface conditioning agents or acids in order to make the surface more receptive to adhesion for dental restorative materials.

Development of adhesive dental materials

Epoxy resins were first synthesized in 1937 by Pierre Caston in Zurich, Switzerland.[91] These materials set with the lowest percentage of volumetric shrinkage of any resin yet developed, and produced the strongest and most permanent adhesive bonds of any known resin. They are used for bonding of components in aircraft, missiles, and spacecraft.[91]

The advent of epoxy resins for industrial use has led to the possibility of employing these adhesive materials in dentistry.

In 1956 Bowen[92] conducted studies on the adhesion of epoxy resins to tooth structure. Both shear and tensile loads were employed to measure the force required to separate the material from the tooth surface. Results showed that the bond strength averaged 300 psi on dry untreated tooth surfaces.

Sadler[93] in 1958 tested several commercial industrial adhesives to determine the feasibility of bonding metal attachments directly to the teeth, thus eliminating bands completely. All of the adhesive materials tested exhibited

a lack of adhesion to metal brackets, and none was capable of bonding the metal attachments directly to the tooth surface with the stability necessary for active tooth movement.

In 1965 Lee[91] tested the adhesion of an epoxy resin by placing a drop of the material on wet and dry tooth surfaces and allowing it to cure at room temperatures. After curing, the specimens were immersed in distilled water at 37°C for 24 hours, after which time the epoxy resin either floated off the tooth surface or was dislodged with thumb nail pressure.

Newman[7] in 1966 reported using bandless orthodontic brackets cemented with an experimental epoxy-polyamide adhesive to tooth surfaces. The bracket loosened after four to six months; however, active treatment was required for only three months.

Recently, Lee[48] reported that blends of epoxy resins cured with tertiary amines appeared promising for dental use. Tests conducted by these formulations showed that they had good reactivity rates, cured to tough hard resins with high tensile and compressive strengths, and possessed both a low volumetric shrinkage and good adhesive strength.

Bowen[94] has stated that "although clinical restorations based upon epoxy resin formulations are being placed in the mouth on an experimental basis, problems remain to be

solved before they can be considered for general use by the practitioner."

Another adhesive system considered for dental use is the akylcyanoacrylate materials.

In 1965 Berstein[6] attempted to lute an orthodontic bracket directly to the tooth surface with a cyanoacrylate adhesive. It appeared that water penetration eventually separated the bond between the tooth surface and the adhesive material.

In 1966 Takeuchi et al[11] conducted a clinical study to ascertain the adhesive quality of an cyanoacrylate and methylacrylate resin when placed in pits and fissures of non-carious permanent first molars in 135 grade school children. After six months, the adhesive material remained in 77 per cent of the teeth, and after nine months, 46 per cent of the teeth still retained the adhesive.

In the same year, Khowassah and Sahs[44] investigated in vitro the sealing property of methyl-2-cyanoacrylate in 36 extracted human teeth with an aqueous five per cent eosin dye solution. The teeth were alternately thermal cycled 15 times in 70°C and 3°C dye solutions for one-minute intervals. Examination under a dissecting microscope revealed only a trace of dye penetration with the cyanoacrylate adhesive material. The investigators concluded that the methyl-2-cyanoacrylate presented promising sealing qualities.

Using a modified T-peel test, Blair[95] determined the adhesive characteristics of a polyester adhesive, an epoxy resin, and a cyanoacrylate adhesive. Of these materials the cyanoacrylate adhesive provided the best metal-to-metal and metal-to-acrylic resin bonding.

Miscellaneous adhesive systems have been suggested for possible use as adhesive dental materials.

In 1964 Newman[4] suggested that adhesive materials containing such groups as -OH, $-COONH_2$, and -C=N are strongly polar and tend to promote adhesion.

Masuhara et al[43] in 1965 experimented with the trialkyborons as initiators of polymerization of self-curing resin materials. Measurements of setting time and bond strengths carried out on ivory teeth instead of human teeth showed the trialkyborons to decrease setting time and increase the bond strength of self-curing resin materials.

Carderelli[96] reported on the research undertaken to study the remarkable ability of the sea barnacle to adhere to surfaces in an aqueous salt water environment. The question was raised as to whether the barnacle might prepare the surface for attachment by secreting a corrosive or acidic substance which would attack or etch the surface, resulting in a mechanical bonding. The feasibility of developing a dental adhesive system using a similar mechanism is being studied.

In 1968 Smith[47] reported on a new carboxylate dental cement composed of polyacrylic acid liquid and a modified zinc oxide powder which exhibited "superior" adhesion to enamel when compared to other commercial cements. Adhesion is said to be achieved by chelation of the calcium within the enamel or dentin by the polyacrylic acid. The data reported indicated that the new carboxylate cement possessed strengths comparable to other cements, produced little irritation of pulpal and oral tissues, and had superior adhesion to enamel. Adhesive values measured on a tensile test apparatus revealed mean values above 1250 psi after storage in water for 24 hours. After two months immersion in water, only a 10 per cent reduction in bond strength was noted.

Swartz, Phillips, and Norman[97] also compared the adhesion of this same carboxylate cement to bovine enamel and dentin with that of zinc phosphate cement. Adhesion was measured under dynamic tensile loading. Adhesive values for the carboxylate cement on enamel averaged 177 psi and 311 psi for 24 hours and three months, respectively; on dentin the average values were 142 psi and 212 psi for 24 hours and three months, respectively. Adhesion values for the zinc phosphate cement were only 59 psi and 74 psi on dentin and 76 psi and 118 psi on enamel when stored for 24 hours and three months, respectively. Thermal cycling

2500 times before application of the tensile load reduced the adhesive values of the carboxylate cement to 154 psi on enamel and 93 psi on dentin.

In 1969 Friend[98] reported good adhesion to dry cavity preparations when a polycarboxylate cement was used as a cavity liner. Also good adhesion of this material was found in a substantial number of damp preparations.

Mortimer and Tranter[99] in 1969 compared the physical properties of two commercially available polycarboxylate cements with those of other conventional dental cements. Adhesion tests were conducted by cementing small stainless steel buttons to enamel surfaces of teeth stored in 70 per cent alcohol. The adhesive bond was measured on an Instron machine using a tensile load. Erratic results were obtained with the polycarboxylate cement. No evidence was found to support the chelation mechanism for increased adhesion with this cement.

Mizrahi and Smith[100] in 1969 conducted a laboratory investigation to develop and standardize a technic for measuring the adhesion of the polycarboxylate cement, Durelon. The adhesion of an orthodontic button cemented to the labial surface of a tooth was measured using a tensile load for tensile and shear testing. The specimens were stored for 48 hours in distilled water prior to testing the bond strength of the cement. Results revealed "superior" adhesion

of the carboxylate cement to enamel surfaces when compared to a conventional zinc phosphate cement. The majority of failures occurred within the cement itself, indicating that the adhesive bond of this material was stronger than its tensile strength.

In a subsequent study, Mizrahi and Smith[101] studied the bond strength of the carboxylate cement in relation to a number of factors considered important with respect to the clinical application of this material. Laboratory data provided the following results: (1) the cement offered the same resistance to either tensile or shear force, (2) prolonged immersion in water did not have an adverse effect on the adhesive bond, (3) a one per cent solution of phosphoric acid left on the enamel surface for five minutes did not increase the adhesive bond strength of this material, (4) saliva contamination reduced its bond strength, and (5) thermal cycling did not significantly reduce the bond strength of this material.

Grieve[102] in 1969 investigated the bond strength of zinc oxide eugenol, zinc phosphate, and polycarboxylate cement for luting a full cast gold crown. He found that the bond strength of the polycarboxylate cement was similar to that of zinc phosphate cement; this was contrary to the findings of Smith,[47] who reported that the polycarboxylate cement had much greater retentive ability than zinc

phosphate cement. There was no correlation between the low compressive strength of the polycarboxylate cement and its bond strength. However, as expected, a correlation did exist between the compressive strength and bond strength of zinc phosphate and zinc oxide eugenol materials.

In 1969 Buonocore and Casciani[49] tested *in vitro* the sealing quality and adhesion of certain urethane-methacrylate compounds to enamel and dentin surfaces. None of the materials reported in this study demonstrated adhesion to tooth structure after one-week immersion in water. Marginal leakage tests with one of the compounds revealed a complete absence of basic fuschin dye penetration around the marginal areas of the restorations. However, the authors noted that this was due to the fact that the material became tightly adapted to the walls of the cavity preparation as a result of increased expansion from water sorption. It was not due to physical or chemical bonding of this material to the tooth surface.

Newman[9] in 1969 reported on several resin systems investigated for use as orthodontic adhesives for attaching bandless brackets. He found that cyanoacrylates and polyurethanes were unsatisfactory because of problems of manipulation and hydrolysis. Acrylic adhesives with lower-molecular weight polymers appeared to be promising for use as an adhesive for luting orthodontic attachments. They

possessed a higher solid content to minimize shrinkage and lower viscosity to provide better wetting. The reinforced fillers such as epoxy or vinyl silane treated glass rods and beads, or fibers incorporated into resin systems were disappointing with respect to improving adhesion.

Lee and Swartz[15] in 1970 conducted a laboratory study to evaluate a urethane repolymer for use as a pit and fissure seal and in posterior teeth. Tests on extracted human teeth showed that: (1) adhesive strengths of 1300 psi were attained, (2) no leakage of isotope was observed on autoradiographs, and (3) intimate contact between the urethane material and the fissured walls of the tooth was observed through the scanning electron microscope.

Adhesive liners

Phillips[70] has suggested the possibility of using an adhesive liner which could bond directly to the tooth surface and final restorative filling material.

Swartz and Galligan[45] in 1967 reported that thin layers of absorbed adhesive-promoting materials, surface conditioners, and thick adhesive liners promoted adhesion to teeth. Among conditioners, the carboxylic acids were the most promising for use with acrylic resin restorations. Several polyurethane compounds formed *in situ* on teeth under room conditions were firmly attached even after water immersion. These materials could be easily applied to the teeth,

rapidly cured, and possessed good color. They were resilient and offered exceptional promise as adhesive liners for acrylic restorative systems.

In 1968 Patrick and Kaplan[46] developed a rubbery liner composed of a long series of polymers using acrylonitrile-ethyl acrylate and glycidyl acrylate for use in pretreatment of the tooth surface for enhancing the adhesion of an experimental resin material.

A punch shear test was employed for measuring the force necessary to punch the plug of experimental material out of a hole drilled through a slice of dentin. The use of the intermediary liner prior to placing the resin appeared to improve shear strength values.

Adhesion was also increased when the tooth surface was coated with silane prior to placing the intermediary liner. The silane coating provided improved moisture resistance when the specimen was exposed to a 37°C saliva bath over prolonged periods. It appeared that the laminated system of silane coating of the tooth surface, the rubbery intermediary liner, plus the experimental resin, provided a significant improvement in bond strength.

In 1970 Lee et al[50] evaluated an elastomeric polyurethane adhesive dental primer used in conjunction with a high strength composite restorative resin material. Adhesion to bovine enamel and dentin was evaluated by means

of a tensile test. Tests were conducted after storage in water at 37°C and after thermal cycling while under a constant load. The adhesive system was also placed in non-undercut preparations in dogs' teeth and in 150 restorations placed in human beings. Laboratory data showed bond strengths of 1500 psi. Thermal cycling 1000 times under a constant load of 200 psi did not reduce the bond strength. Results of *in vivo* testing revealed that the adhesive system could be retained to the shallow non-undercut preparations without loosening which was evident in the control teeth without the adhesive polyurethane primer.

Surface conditioning agents

Buonocore[38] has suggested the possibility of altering the tooth surface with conditioning agents in order to produce a new surface to which materials might adhere.

In 1952 McLean and Kramer[103] evaluated the pulp response and cavity sealing property of a sulfinic activated resin, Sevriton, and the cavity sealer or surface conditioning agents provided by the manufacturer. The cavity sealer, which is applied to the tooth surface prior to placing the resin, was found to contain a high molecular compound dissolved in methacrylic acid. It possessed both a low surface tension and affinity for hard tooth structure. It formed a polydimensional structure upon

polymerization. No difference was observed in the pulp response to the Sevriton resin and its cavity sealer when compared to other resin systems or with the Sevriton resin without the sealer. Investigations of the cavity sealing property of the resin by dye penetration method revealed that an effective seal was obtained with the resin plus cavity sealer.

Subsequent histological studies by the same investigators[104] revealed an altered staining reaction of three microns in the dentin when the cavity sealer was applied. This altered zone of dentin was not observed in specimens without the cavity sealer, which suggested the possibility of the sealer providing molecular attachment between the resin material and dentin.

Analysis of the Sevriton cavity sealer indicates that it contains 5-10 parts of phosphoric acid ester; 5-10 parts of methacrylic acid; and 80-90 parts methyl methacrylate with perhaps a trace of methacrylic anhydride.[51]

Swartz and Phillips[105] in 1955 evaluated <u>in vitro</u> the adhesive characteristic of various resin filling materials and cavity sealers to enamel and dentin. The results demonstrated that the cavity sealers improved the adhesion of acrylic resin to enamel surfaces by wetting and penetrating into the surface irregularities.

In 1960 Kramer and Lee[106] studied the nature of the chemical component of the Sevriton cavity sealer. It was discovered that the glycophosphoric acid dimethacrylate plus the methacrylate monomer were the two components of the cavity sealer responsible for the altered staining in the dentin as observed in earlier studies. When the resin was applied over the sealer, part of the sealer dissolved in or mixed with the monomer of the acrylic resin.

In 1965 Swartz[79] stated that the cavity sealers provided by the manufacturers of restorative acrylic resins helped to adapt the resin to the walls of the cavity preparation. Because of its low surface tension or energy, the sealer readily flowed into the minute irregularities of the preparation. In addition, the sealer contributed to cleaning the prepared cavity so that the resin "wetted" the walls of the preparation more readily and efficiently.

Peterson[69] reported that in adhesion tests, Sevriton resin and its cavity sealer demonstrated greater resistance to separation under a tensile load than other resin systems. After 24 hours storage in distilled water, Sevriton resin and its cavity sealer separated on an average of 275 psi, while without the sealer, the values dropped to 142 psi. After one-week storage in water, the adhesion values decreased to 226 psi with the cavity sealer, and to 100 psi without the sealer. This decrease was thought to

be due to the penetration of water between the resin material and dentin surface.

When Bowen[92] studied the adhesion of epoxy resins, he noted that when the tooth surface was pretreated with ethylene diamine tetraacetate (EDTA), the bond strength of the epoxy resin improved from 300 psi on untreated surfaces to 740 psi on the treated surfaces.

In 1963 Matsui and Minogughi[66] observed an increase in the adhesion of a methyl methacrylate resin and an experimental resin on tooth surfaces treated with either a vinyl trisersorve-estersilane, methacrylate chromic chloride, or glycophosphoric acid dimethacrylate. The investigators postulated that a chemical bond might take place between the tooth structure, the vinyl silane, and the methyl methacrylate resin. The $-CH_3$ radical of the vinyl silane might possibly bond with the $-CH_3$ radical of the methyl methacrylate. The -OH radical in the apatite crystal of tooth structure would then be replaced with the -Si- of the vinyl silane to form a Si-O or Si-H bond.

In 1965 Bowen[107] conducted an extensive five-part investigation to determine the adhesive bonding of various materials to hard tooth tissue. He investigated the hypothesis that a surface-active comonomer would provide improved water-resistant bonding between a self-curing resin and human dentin. The surface-active comonomer was

the addition-reaction product of N-phenyglcine and glycidyl methacrylate (NPG-GMA) which was applied over the tooth surface prior to placing the resin. The specimens were subjected to tensile loads in order to determine the force necessary to break the bonds apart. Results demonstrated that the NPG-GMA comonomer, when used as a coupling agent between dentin and acrylic resin, repeatedly gave better bonding strengths than specimens without the comonomer.

Bowen[54] then attempted to increase the adhesion values obtained with the surface-active comonomer by pretreating the dentin with either sodium hydroxide or hydrochloric acid. Pretreating the dentin surface with the dilute solution of hydrochloric acid gave an average adhesion value of 810 psi as compared to only 630 psi when the NPG-GMA was used without pretreating the dentin with acid. Pretreating the tooth surface with sodium hydroxide gave higher values of 950 psi.

Subsequently, Bowen[108] pretreated dentin, enamel, and fluorapatite with a 10 per cent solution of EDTA before applying the surface-active comonomer and self-curing resin. After such treatment, the bond strengths for dentin, enamel, and fluoroapatite were 1,100 psi, 777 psi, and 1,110 psi, respectively. Testing the effect of the NPG-GMA surface-active comonomer on the organic constituents in enamel and dentin, Bowen concluded that the

improved bond strength with NPG-GMA was due primarily to a mechanism involving the mineral phase and not the organic phase within the tooth structure.

In 1965 Swartz and Galligan[109] conducted a series of tests to develop a surface conditioning agent for increasing the adhesion of a polymethacrylate resin. Many conditioning agents were applied to the polished surfaces of human and bovine enamel and dentin. A polymethacrylate resin was then applied and allowed to cure for 18 hours. Adhesion was measured by using a "spot scraping test." After soaking in distilled water for 24 hours, only Gelva C-5 and V-10 showed any degree of adhesion; however, these two conditioning agents failed to maintain lasting adhesion after 48 hours.

In 1970 Termini et al[60] studied surface treatment of bovine enamel and dentin with various chelating agents in order to obtain enhanced bonding between tooth surface and acrylic restorations. Bovine enamel and dentin were pre-treated with a five per cent aqueous tetrahydrofuran-2,3,4,5-tetracarboxylic acid dianhydride (TTAD) for 10 seconds before applying the acrylic resin. Tensile adhesion tests yielded enamel-acrylic bond strength values up to 850 psi. One-month water storage did not destroy the adhesion of the resin to the tooth surface.

Surface etching with acid

Altering the tooth surface by etching with either

inorganic or organic acids has been considered as another approach for enhancing the adhesion of dental materials.

Newman[9] recently stated that "by pretreating the tooth surface with phosphoric acid, one can convert the normally hydrophobic, low energy surface of tooth structure to a more wettable, hydrophilic high energy surface ready to accept a low energy adhesive resin."

Various optical devices have been used to observe the effect of acid etching of tooth structure.

In 1932 Kanthak and Benedict,[110] using a simple optical microscope, studied the effect of various acids at varying concentrations on the enamel surfaces of extracted human teeth. Time of exposure of the acids on the enamel surfaces varied from a few seconds to several minutes. The investigators observed a "honeycomb" structure with small radiating structures running from each enamel rod toward other enamel rods.

Sharpe[111] in 1961 studied high resolution microradiographs of five-micron-thick ground sections of human enamel cut in various planes which have been etched with different acids at varying pH's. He noted that when the acid attack was parallel to the enamel prisms, a honeycomb structure was apparent.

Poole and Johnson[112] in 1967 used a scanning electron microscope to compare surfaces of enamel etched with

different dimineralizing agents. Freshly extracted human molar teeth were treated for five hours with EDTA, formic, lactic, and hydrochloric acid. Results revealed a variation from shallow depressions to distinct holes 3-4 microns in diameter, surrounded by walls one micron thick. Etching of enamel surfaces cut transverse to the prisms revealed similar features except that the defects produced were deeper. Honeycomb features appeared to be the result of dissolution at the centers of enamel prisms. Each hole was measured at 3-4 microns in diameter with the intervening walls one micron thick. Etching of enamel surfaces cut parallel with the prisms revealed troughs and ridges.

In 1969 Gwinnett[58] observed the histologic changes in the enamel after the application of adhesive conditioning agents. Different concentrations of phosphoric, hydrochloric, and formic acid were applied for one to three minute periods. Optical microscopy, microradiography, and the scanning electron microscope revealed histologic changes varying from mild etching of five microns to a more intense etching of 25 microns with additional widening of prism boundaries in depth beyond the etched enamel. The extent of changes observed depended upon the type and concentration of acid used.

Newman[9] in 1969 studied surface replicas of enamel pretreated with phosphoric acid by interferometer

measurements. A characteristic "pitted prism-end pattern" was observed. Three to six months after removal of a bonded attachment to the acid conditioned surface, the tooth surface resembled its original surface. The acid conditioned pitted pattern had been replaced by a smooth, tightly adhering pellicle of salivary origin.

In 1965 Provenza and Sardena[72] used the electron microscope to study the effectiveness of various debris removal procedures. The electron microscope revealed excessive debris on the enamel surface after operative procedures involved in cutting cavity preparations. Etching with 1/10 N hydrochloric acid succeeded in removing the smaller particles of debris; however, the larger particles appeared unaffected.

Using a scanning electron microscope, Lee et al[73] also studied the effectiveness of surface treating agents on tooth surfaces. They concluded that removal of the organic debris and subsequent etching with acid appeared to provide a stronger bonding surface, larger surface area, and additional sites for mechanical bonding. Based upon their observations and those of other investigators, the following reagents were classified with respect to their ability to cleanse the cut tooth surface: Good - proteinase enzymes, phosphoric acid, citric acid, and sulphuric acid; Fair - acetic acid, EDTA, and boric acid; No apparent

activity - oxalic acid, hydrogen peroxide, sodium hydroxide, and hydrochloric acid.

Uy and Chang[113] in 1965 investigated the adhesion properties of tooth surfaces by studying the wettability of a number of organic liquids possessing various functional groups. The investigators found that freshly extracted teeth treated with .01 N citric acid on dentinal surfaces exhibited lower contact angles using drops of water. Ring shear test showed an average significant increase in adhesive bond strength of 11.23 pounds for a commercial composite dental resin, Addent. It was concluded from this study that citric acid modified the dentin surface, making it more wettable and thus increasing the adhesion of the dental resin.

In 1966 Newman et al[64] studied the wettability of various prepared tooth surfaces. A Gaertner contact angle goniometer was used to measure the contact angle produced by an epoxy resin on the enamel surface of extracted central incisors. The enamel surface was pretreated with 85 per cent phosphoric acid prior to placing the resin. They observed that the acid conditioning converted a surface on which both water and resin adhesive exhibited a relatively large contact angle to a surface on which water and adhesive exhibited a small contact angle.

Glantz[59] reported that human enamel normally has a low surface energy consisting of organic phases of tooth substance. When the enamel surface was treated with a weak lactic acid solution, the surface became hydrophilic. The author postulated that this was probably due to the fact that the acid dissolved the low energetic organic surfaces and exposed the high energy inorganic crystals.

In 1955 Buonocore[38] explored the possibility of increasing the adhesion of acrylic resin to enamel surfaces by treatment with one of two conditioning agents, a 50 per cent solution of phosphomolydate and an 85 per cent solution of phosphoric acid. Results demonstrated that a drop of acrylic resin placed on the labial enamel surfaces which had been treated with phosphoric acid for 20-30 seconds, remained on the tooth surface an average of 1,070 hours as compared to an average of only 11.2 hours on untreated surfaces. The author postulated that the increased adhesion from the acid etching may have been due to the following: "(1) Increasing the surface area and surface wettability of the tooth surface; (2) exposing the organic framework of enamel which served as a network in and about which the acrylic might adhere to; (3) removing the old, fully reacted inert enamel surface and then exposing a fresh reactive surface more favorable to adhesion; and (4) producing on the enamel surface an absorbed layer of high polar bonding of acrylic resin."

In 1956 Buonocore et al[51] treated dentin surfaces *in vitro* with a seven per cent solution of hydrochloric acid for one minute before placing a standard restorative resin. The acid treatment of the dentin did not increase the adhesion of the restorative resin on the dentin surface. However, an adhesive material made from mixing Sevriton cavity sealer, methyl methacrylate polymer and monomer, two per cent benzoyl peroxide, and freshly prepared para-toluene sulfinic acid did double the adhesive quality of the material on acid-treated dentin surfaces. The bonding also exhibited good resistance to water immersion.

Buonocore and Quigley[52] conducted a histologic investigation to study the area of bonding between Sevriton resin and its cavity sealer on untreated and acid-treated dentin surfaces, and completely decalcified surfaces. Without the use of the sealer, no acrylic resin consistently maintained adhesion on the dentin surfaces. However, when the cavity sealer was applied prior to placing the resin, a thin layer of resin remained bonded to the dentin. Histologic sections revealed the same altered zone of staining in the dentin of 3-10 microns in width as observed by Kramer and McLean.[104]

The application of the cavity sealer to acid-etched and completely decalcified dentin provided greater bond strength besides widening the altered zone of staining.

The investigators suggested that the zone of altered staining might indicate a physical penetration or chemical combination of the sealer with the dentinal organic component.

Swanson et al[53] evaluated *in vitro* and *in vivo* the adhesion of an alkycyanoacrylate on enamel surfaces etched with 85 per cent phosphoric acid for 60 seconds. The *in vivo* results demonstrated an increase in adhesion but the adhesion decreased when the specimens were subjected to moisture.

In a clinical study in 1967 Buonocore and Cuerto[12] investigated the sealing of pits and fissures of teeth with an adhesive resin, methyl-2-cyanoacrylate. Prior to placing the adhesive material, one to two drops of 50 per cent phosphoric acid in which seven per cent by weight of zinc oxide was dissolved was applied to pit and fissure regions with a cotton pellet. Six months examinations revealed that 80 per cent of the teeth were still completely covered with the adhesive. After one year, 71 per cent of the teeth were still completely covered. No controls to measure the duration of the adhesive on non-acid conditioned surfaces were included in this study.

In 1967 Pitt[114] reported on the adhesion of two commercial resins, Addent and Bonfil, to acid-treated dentin surfaces. A 0.1 N aqueous solution of citric acid

was applied for five minutes over dentin surfaces prior to placing the resin. Increased adhesion was obtained. Electron micrographs revealed that citric acid augmented the mechanical adhesion of the resin materials by removing and releasing debris from the dentinal tubules, and possibly exposing the tubule openings to accept the dental resin. The acid-treated surface delayed, but did not preclude, the penetration of water into the dentin-resin interface.

Gwinnett and Matsui[55] in 1967 investigated the physical relationship between several adhesive materials and conditioned enamel surfaces. One-half of the specimens were etched for seven seconds with 0.1 N hydrochloric acid prior to placing a restorative resin, Sevriton. Sectioned specimens were embedded and decalcified. When the specimens were examined under an electron microscope, filamentous "tag-like" extensions of 15-20 microns in length were seen at the interface where the resin material contacted the etched enamel surface. No tags of acrylic resin were observed on non-etched enamel surfaces. The investigators suggested that the acid etching created more surface area for bonding and opened more spaces into which the adhesive could flow and "encapsulate" the crystallite component of enamel.

In 1968 Buonocore et al[57] also conducted an investigation to determine whether the improved bonding of resin

materials to acid-conditioned enamel surfaces might be related to their penetration into the enamel surface. The enamel surfaces of extracted caries-free human teeth and deciduous anterior bovine teeth were pretreated for 60 seconds with a 50 per cent solution of phosphoric acid. Two commercial anterior restorative resins, Bonfil and Sevriton, and two commercial composite resins, Dakor and Addent, were placed over the treated and untreated enamel surfaces. At the end of one year the teeth were immersed for three days in 0.5 per cent basic fuchsin dye containing 19 u c/ml of radioactive sulfur-35 as $SO4^{35}$. A lack of penetration of the radioactive dye between the enamel-resin interface of both human and bovine teeth was observed. Study of resin penetration into the acid-conditioned enamel surface revealed prism-like tags as observed by Gwinnett.[55]

In the same year Mulholland and DeShazer[56] studied the effects of acid pretreatment solutions of various molarity and pH on the bonding of Addent 35 when used for direct cementation of orthodontic brackets to the surfaces of freshly extracted human anterior teeth.

Two monovalent acids, hydrofluoric and hydrochloric, and two polyvalent acids, phosphoric and aspartic, were applied to the enamel surface prior to placing the bracket and resin. The strengths of the bonds were measured by a vertical tensile stress apparatus. The specimens were tested at one-hour and four-day intervals.

The results of these tests indicated that although molarity had no significant effect upon bond strength, a definite correlation did exist between bond strength and a reduction in pH. With the polyvalent acids no demonstrable increase in bond strength was noted above a pH of two. The investigators noted that treatment with the monovalent acid, hydrofluoric, gave a significant increase in bond strength at a pH of four when compared to other acids. For example, treatment with phosphoric acid increased bond strength only when the pH was lowered to two.

Newman[8] in 1968 studied the feasibility of replacing orthodontic metal banding of teeth with a system of plastic attachments. Tooth surfaces of extracted teeth were pre-treated with phosphoric acid prior to applying the acrylic adhesive and polycarbonate bracket. The bonded specimens were immersed in distilled water at 37°C and stored for 30 days. A modified shear force was performed and the stress was applied at a constant rate of one pound per minute until bond failure occurred. Water immersion substantially reduced the bond strength. However, conditioning of the enamel with acid improved the adhesion values to 710 psi as compared to only 61 psi on untreated surfaces.

In 1968 Hanke[42] employed several resin systems and various tooth surface conditioning agents in experiments designed to develop a simple screening test for assessing the relative adhesion of dental restorative materials.

During these experiments, two experimental composite resins and a commercial sulfinic acid restorative resin, Sevriton, were subjected to storage in water, temperature and mechanical stress cycling. The adhesion was measured by means of a tensile load applied at a cross head speed of 0.30 inches per minute until the bond was ruptured. Citric acid, phosphoric acid, hydrochloric acid, EDTA, and Eastman 910 were conditioning agents placed on bovine dentin prior to placing the Sevriton resin. None of the Sevriton-citric acid treated specimens survived the first mechanical stress cycle. Pretreatment of the dentin with phosphoric acid did not significantly improve adhesion. However, a statistically significant increase in adhesion with the Sevriton resin was obtained when the dentin surfaces were treated with either hydrochloric or citric acid. The investigator did not test the adhesion of Sevriton to enamel pretreated with the conditioning agents.

Doyle[2] recently described the "Etched Restoration Technic" involving fractured incisors. He suggested that this technic be used where fractures are too large to be adequately or esthetically recontoured with a dental stone and too small for the placement of a pin reinforced resin. The procedure involves isolating the unanesthetized tooth with a rubber dam and applying a saturated cotton pellet

of 50 per cent phosphoric acid for 45 seconds over the fractured area. The acid is flushed with water and the area dried with air. A cavity primer is then applied and increments of resin are built up. The restoration is finished with burs and polished with pumice in a prophylaxis cup.

Laswell, Welk, and Regenos[3] studied the effectiveness of acid etching on the retention of acrylic resin. Recently extracted maxillary incisors were separated into three groups. The labial surface of group one was cleaned only with flour of pumice; group two was ground with a diamond stone; and group three was etched with a 50 per cent solution of phosphoric acid for 45 seconds. The specimens were stored for one hour, 24 hours, and one week. The adhesion of Sevriton resin was measured on an Instron machine by applying a tensile load at a rate of 0.050 inches per minute.

At one hour the force required to separate the acrylic resin from the tooth surface was comparable for surfaces treated with either the phosphoric acid or the diamond stone.

After one week, only three out of ten of the unaltered surface specimens retained attachment of the resin, while the resin applied to the etched surfaces appeared unaffected by time of storage. All acid-etched specimens exhibited

cohesive or adhesive-cohesive breaks, indicating that the strength of the bond exceeded the tensile strength of the material.

From this study it was concluded that phosphoric acid pretreatment of the enamel surface improves the adhesion of acrylic resin to the tooth surface. A clinical technic using this principle to restore the fractured incisal angle of maxillary anterior teeth without the use of pins, and to correct developmental defects on the labial surfaces of anterior teeth was presented. The authors did not recommend the use of the Sevriton cavity sealer.

In 1970 Buonocore[13] reported on a new liquid adhesive composed of three parts by weight of the reaction product of bisphenol A and glycidyl methacrylate and one part by weight methyl methacrylate monomer when exposed to ultra-violet light to induce polymerization. It was stated that this material provided complete protection against pit and fissure caries when applied to permanent and deciduous teeth. The enamel pit and fissure areas had been pretreated with one to two drops of a 50 per cent aqueous solution of phosphoric acid before applying the adhesive material. After one year, of the 200 pits and fissures sealed with this new adhesive material, only one became uncovered. This material also provided 100 per cent caries protection, whereas 42 per cent of the matched contra-lateral control teeth had developed caries.

Ripa and Cole[14] in 1970 reported that after 12 months, there had been an 84.3 per cent caries reduction in permanent and deciduous posterior teeth when the occlusal areas had been sealed with an adhesive mixture of methyl-2-cyanocrylate and powdered filler. After one year approximately one-third of the teeth available had become uncovered, one-third were partially covered, and one-third were completely covered with the adhesive material. The teeth that were covered with the adhesive sealant were conditioned for adhesion by etching for 30-40 seconds with a 50 per cent aqueous solution of phosphoric acid before applying the adhesive material. The authors postulated that preconditioning the tooth with acid increased the mechanical or chemical bond of the adhesive material to the enamel surface of the tooth.

The review of the literature indicates a need for a comprehensive laboratory study to determine if etching of enamel surfaces with phosphoric acid will increase the retention of dental restorative and luting materials. Some of the reported investigations were of short duration, included many variables, lacked adequate controls and numbers, and presented conflicting data. Many studies lack information concerning what effect thermal and mechanical stress cycling would have on the adhesive bond of dental materials placed on acid-etched tooth surfaces. No study

up to this time has measured the adhesion of the polycarboxylate cement, Durelon, to enamel etched with 50 per cent phosphoric acid. Also there are no studies which have assessed the marginal seal of conventional unreinforced restorative resins to acid-etched Class V cavity preparations in extracted human teeth.

METHODS AND MATERIALS

Substrate

Extracted bovine mandibular incisors were selected as the substrate for testing the adhesion of a conventional unreinforced restorative resin and a polycarboxylate cement on etched and unetched enamel surfaces. The bovine incisors were extracted with a dental forcep after the animals had been slaughtered in a nearby meat packing house.[+] The teeth were kept in a diluted solution of formalin for approximately five hours and then rinsed and scrubbed in running tap water and transferred into a beaker of distilled water and frozen until employed in the study.

The procedure for preparing and mounting the teeth and test specimens and for measuring the adhesion of the test materials is the same method and procedure developed and used by Hanke[42] in a previous study.

The bovine incisors were prepared by separating the crown and root with a band saw. The pulps were mechanically removed with a gutta percha point spreader. The labial enamel surfaces were flattened by grinding on a wet rotary

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[+]Stark and Wetzel Co., Inc., Indianapolis, Indiana

wheel using 80 grit silicon carbide paper.* The teeth were then placed with the labial surface down flat on a glass cement mixing slab and aluminum rings (inside diameter 20.5 millimeters and height of 10 millimeters) placed around each tooth. The aluminum rings lubricated with vaseline on the inside to facilitate removal were filled with a self-curing methyl methacrylate resin.** When the resin material had polymerized (30 minutes), the aluminum rings were removed. The exposed labial enamel surfaces of the mounted bovine incisors were then finished with a wet 400 grit silicon carbide paper* attached to a rotary wheel. The mounted teeth, as shown in Figure 1, were stored in distilled water. When the teeth were ready for use, the enamel surfaces were dried with air using a chip blower.

Surface Conditioning Agent

A 50 per cent aqueous solution of phosphoric acid was applied with a pledget of cotton for 60 seconds to the enamel surfaces of the test specimens to be etched. The acid was flushed with copious amounts of running tap water and the etched enamel surfaces dried with air using a chip blower.

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* Redi-Cut, The Carborundum Co., Chicago, Illinois.

** Formatray, Kerr Mfg. Co., Detroit, Michigan.

Part I - Adhesion of Direct Filling Resin

The direct filling resin material used in this study was a sulfinic acid activated unreinforced poly(methyl) methacrylate resin.[+] The adhesion of this material was tested on etched and non-etched enamel surfaces, both with and without the cavity sealer supplied by the manufacturer.[+]

A total of 414 test specimens were placed into 39 groups which were divided into four principal groups: in Group I the enamel surface was pretreated with the phosphoric acid and the cavity sealer before applying the resin; in Group II the enamel surface was pretreated with only the phosphoric acid before applying the resin; in Group III the enamel surface was treated with only the cavity sealer before applying the resin; and in Group IV (Control) the resin was applied on the polished enamel surface.

A split silicon ring matrix with an outside diameter of 15 millimeters, an inside diameter of 6.85 millimeters, and a height of four millimeters was used to confine the resin material. A brass ring was slipped over the outside of the silicon matrix to maintain its dimension. The matrix was carefully positioned over the enamel surface and held in place by finger nail polish lightly painted on the under-surface of the silicon matrix.

[+] Sevriton Simplified, Amalgamated Dental Trade Dist., Ltd., London, England.

In Groups I and III the cavity sealer was applied using a fine camel hair brush. The monomer liquid and polymer powder were placed in two separate dappen dishes. With another fine camel hair brush beads of resin picked up by first dipping the brush into the monomer and then into the polymer were placed onto the enamel surface and built up until the silicon matrix was filled. Additional amounts of resin were mixed in another dappen dish according to the manufacturer's instructions. This mix was placed into a circular cavity (.25 inches in diameter) drilled in a brass ball (.5625 inches in diameter). The brass ball with the cavity filled with resin was carefully positioned over the resin in the silicon matrix and the resin allowed to completely polymerize for 20 minutes. (A specimen is shown in Figures 2 and 3.) The brass ring and silicon matrix thus were removed and the test specimens were stored in a glass container of distilled water at 37°C.

Method of Testing

The following tests were conducted to determine the effect of storage time in water, temperature stressing, and intermittent tensile stressing on the adhesion of the commercial direct filling restorative resin material on acid-etched and non-etched enamel surfaces.

Storage in Water

The acrylic resin test specimens (Groups I, II, III,

and IV) were stored in distilled water at 37°C for 24 hours, 30 days, and six months. At completion of the respective storage times the test specimens were subjected to a tensile test to measure the adhesive bond strength of the resin material. Each specimen was held in a special jig mounted on a Rhiele testing machine as shown in Figure 4. A tensile load was applied at a cross head speed of 0.030 inches per minute until bond failure occurred.

Temperature Stressing

At completion of storage times of 24 hours, 30 days, and six months in distilled water at 37°C, the acrylic resin test specimens (Groups I, II, III, and IV) were subjected to thermal stressing. Using the automatic temperature cycling apparatus shown in Figure 5, the test specimens were alternately cycled 500 times between two water baths. One bath was maintained at 10°C $\pm$ 5 and the other bath at 50°C $\pm$ 5. The immersion time in each bath was 30 seconds. At completion of the temperature cycling the bond strength of each test specimen was measured by applying a tensile load at a rate of 0.030 inches per minute.

Mechanical Stressing

At completion of storage times of 24 hours, 30 days, and six months the test specimens were subjected to intermittent tensile stressing.

Each test specimen (Groups I, II, III, and IV) was subjected to a load of 300 psi at a cross head speed of 0.50 inches per minute. Upon reaching the 300 psi level the load was released and reapplied at the same rate. Upon completion of stress cycling 60 times, each specimen was then subjected to a tensile load at a rate of 0.030 inches per minute until bond failure occurred.

Temperature and Mechanical Stressing

One group of acrylic resin test specimens (Group I) treated with both the phosphoric acid and cavity sealer was subjected to both temperature and intermittent tensile stressing upon completion of storage times of 24 hours, 30 days, and six months. First, the test specimens were thermal stressed 500 times between two water baths at a temperature differential of 40^{o}C. Immersion time was 30 seconds. At completion of the temperature stressing the specimens were subjected to intermittent tensile stressing. The load and rate were the same as above for the test specimens subjected to only stress cycling. At completion of the intermittent tensile stressing, the test specimens were loaded at a rate of 0.030 inches per minute until failure occurred. Every specimen was examined under a dissecting microscope at 20 power to determine the type of bond failure.

Part II - Marginal Leakage of Direct Filling Resin

A limited number of extracted human teeth were restored with the same commercial direct filling acrylic resin used in Part I of this study, and the effect of temperature cycling on the marginal seal of this material as related to etching the cavity preparation with 50 per cent phosphoric acid was investigated.

Class V cavity preparations were cut in the middle third of the labial surface of crowns of 40 extracted human canine and bicuspid teeth. The teeth had been previously stored in tap water. The cavity preparations were prepared using a 557 carbide bur in an air rotor and finished with a 557 steel bur using a conventional low speed hand-piece and with a Wedelstadt chisel hand instrument.

Twenty preparations were etched with a saturated cotton pledget of 50 per cent phosphoric acid for 60 seconds, rinsed with running tap water, and then dried with air using a chip blower.

The other 20 prepared teeth not etched with acid were also rinsed in running tap water and dried with air.

The cavity sealer was applied over the enamel walls of both etched and non-etched preparations. The acrylic resin was inserted into the preparations using the non-pressure bead technique. The protective film supplied by the manufacturer was placed over the restorations during polymerization. Fifteen minutes later the restorations

were finished using sandpaper discs lubricated with vaseline.

The 40 specimens were divided equally into two groups. Each group consisted of 10 etched and 10 non-etched specimens. The Group I specimens were placed in distilled water and stored for one week at 37°C. Group II specimens were alternately thermal stressed cycled 2500 times between two water baths at a 40°C temperature differential. The immersion time was 30 seconds. It took one week to complete the 2500 cycles.

Radioactive calcium (Ca^{45}) was employed to assess the marginal seal of the restorations. The laboratory technique is the same method used in previous studies.[28,29,35,69]

The 40 teeth were sealed with clear finger nail polish so that only the periphery of the restorations and tooth structure was exposed. Tin foil was wrapped around each tooth so that only the restoration was exposed and the edges of the tin foil were sealed with clear finger nail polish. The teeth were immersed in a solution of radiocalcium 45 (.1mc/ml) for two hours at room temperature. Upon removal they were rinsed under running tap water for one hour. The teeth were scrubbed with a detergent solution before and after the tin foil was removed.

The teeth were longitudinally sectioned in half using a Gillings Hamco sectioning machine. The tooth sections

were placed, cut surface down, on an ultra high speed dental X-ray film which was supported by a plastic slab. The tooth was held in position by means of a rubber band. (See Figure 6.)

The assembly was wrapped in tin foil and placed into a light proof container for 17 hours. The film was processed and developed with routine dark room procedures. The resultant autoradiographs were visually examined for penetration of the isotope at the margins of the restorations.

Part III - Adhesion of Polycarboxylate Cement

The adhesion of a new commercial polycarboxylate cement composed of a polyacrylic acid liquid mixed with a modified zinc oxide powder[+] was also tested on both acid-etched and non-etched bovine enamel surfaces. One hundred and eighty test specimens were prepared and divided into two groups. In Group I the enamel surface was etched with 50 per cent phosphoric acid for 60 seconds before applying the cement. In Group II (Control) the enamel surface was not treated with acid before applying the cement. A 1:1 powder-liquid ratio was carefully proportioned out on an analytical balance. The powder was incorporated into the liquid and mixed on a paper slab for 30-40 seconds with a

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[+] Durelon Carboxylate Cement. Premier Dental Products Co., Philadelphia, Pa.

cement spatula. The material was placed onto the enamel surface and filled to the height of the silicon-brass ring matrix. The circular cavity in the brass ball was then filled with the remainder of the material and carefully positioned over the silicon matrix. The mounted test specimens were immediately placed into a humidor at 37°C for 30 minutes and immersed in a glass container of distilled water. Specimens were stored at 37°C for 24 hours, 30 days, and six months. The method of testing the adhesion of the polycarboxylate cement was the same method used on the direct filling acrylic resin test specimens. However, during the mechanical stress cycling, the pre-set tensile load value was 100 pounds per square inch (psi) for the polycarboxylate test specimens. At completion of the intermittent tensile stressing the specimens were loaded at the same rate (0.030 inches/minute) as the acrylic resin specimens until failure occurred.

RESULTS

Part I - Adhesion of Direct Filling Resin

A statistical analysis was performed on the data obtained for 39 groups which were divided into four principal groups (Groups I, II, III, and IV) as dictated by the storage times and testing conditions. The factorial analysis of variance could not be performed on the data because of the marked inequality of variance among the groups, even with the logarithmic transformation of the data. Bartlett's Chi-square test[115] of homogeneity of variance yielded a highly significant Chi-square of 940.51. The Welch Test[116] was used to compare the 39 groups. Results of the Welch Test showed a highly significant F' value of 82.51, indicating a difference among the groups. The Newman-Keul's test[117] was used for individual comparisons among the 39 groups. (See Table XVI)

Storage in Water

The results of adhesion tests conducted on direct filling resin specimens stored for 24 hours in water are shown in Table I and are summarized in Figure 7. These data include the values obtained on enamel surfaces pretreated with the 50 per cent phosphoric acid, the cavity sealer, and the acid and cavity sealer.

Nine out of 16 control specimens (untreated enamel surfaces) in the 24-hour Group IV series separated from the tooth surface during or immediately after insertion into the tensile testing apparatus. The average bond strength was 64 psi. Examination of the specimens under a dissecting microscope indicated that all failed at the resin-tooth-interface.

Pretreatment of the polished enamel surface with the cavity sealer significantly (P=0, 05) increased the average bond strength to 360 psi for the 24-hour-Group III (Sealer) series of test specimens.

The average bond strength was further increased to 581 psi for the 24-hour-Group II series of test specimens in which the enamel surface had been pretreated with the 50 per cent phosphoric acid. A significant difference (P=0.05) was shown by the Newman-Keul's test between Groups II (Acid) and III (Sealer).

An average bond strength of 893 psi was obtained with the 24-hour-Group I (Acid+Sealer) series of test specimens in which the enamel surface had been pretreated with both the phosphoric acid and the cavity sealer before applying the resin. There was a significant difference between Groups I (Acid+Sealer) and III (Sealer) and Groups I and IV (Control) at P=0.05; however, no significant difference was found between Groups I (Acid+Sealer) and II (Acid).

The types of bond failure observed with the Group II (Acid) and III (Sealer) specimens were mostly adhesive-cohesive separations with a few cohesive failures observed with some of the Group II (Acid) specimens. The types of bond failure observed with the Group I (Acid+Sealer) specimens were mostly within the material itself, with a few occurring both at the resin-tooth-interface and within the material.

The data for the 30-day test specimens in Groups I, II, III, and IV are presented in Table II and summarized in Figure 8.

All of the 30-day-Group IV control specimens separated from the enamel surface before insertion into the testing apparatus.

Thirty days storage in water significantly (P=0.05) reduced the average bond strength of the Group III (Sealer) series of test specimens to 164 psi. However, the average bond strength for the 30-day-Group III (Sealer) series of specimens was still significantly higher than for the 30-day-Group IV control test specimens as shown by the Newman-Keul's test in Table XVI.

The average bond strength obtained for the 30-day-Group II (Acid) series of test specimens was 442 psi. There was no significant difference between 24 hours or 30 days

storage in water for the Group II (Acid) specimens in which the enamel surface had been pretreated with phosphoric acid.

The average bond strength obtained for the 30-day-Group I (Acid+Sealer) series of test specimens was 1136 psi. The Newman-Keul's test showed that there was a statistically significant difference between the average bond strengths obtained for the four principal groups which had been subjected to 30 days storage in water.

The types of bond failure observed for the Group I (Acid+Sealer) and II (Acid) test specimens were mostly adhesive-cohesive breaks, while the types of bond failure observed for the Group III (Sealer) and IV (Control) test specimens were adhesive breaks.

Table III shows that results obtained for test specimens in Groups I, II, III, and IV stored in water for six months were comparable to those obtained for the same four groups stored in water for 30 days. A significant ($P=0.05$) difference was noted between the four principal groups.

Temperature Stress

The results of temperature stress cycling of test specimens in Groups I, II, III, and IV immediately following 24 hours, 30 days and six months storage in water appear in Tables IV, V, and VI and are summarized in Figures 7, 8, and 9.

The control Group IV (untreated enamel surfaces) series of test specimens separated during their respective storage periods and therefore could not be subjected to thermal stressing and tensile testing.

Test specimens in Group III (Sealer) stored in water for 24 hours and 30 days either separated during the thermal cycling procedure or during insertion into the tensile testing apparatus before any tensile load could be applied. The type of bond failure observed occurred at the resin-tooth-interface. The resin attachment of some of the six-month-Group III (Sealer) test specimens appeared to be only slightly affected by prolonged storage in water and temperature cycling as shown by the mean value of 54 psi. (See Table VI) However, there was no significant difference between the three different storage periods for the Group III (Sealer) series of test specimens subjected to temperature cycling.

Regardless of storage times, all of the test specimens in Group I (Acid+Sealer) and Group II (Acid) survived the 500 thermal stress cycles at a 40^{o}C temperature differential. The average bond strength values for the Group II (Acid) series of test specimens were 691 psi at 24 hours, 595 psi at 30 days, and 442 psi at six months. The average values obtained were comparable to the values obtained for the Group II (Acid) test specimens not subjected to temperature

stressing. A significant difference (P=0.05) was noted between Group II (Acid) and III (Sealer) and Group II (Acid) and IV (Control), but not between Groups III and IV.

The average bond strength values obtained for the Group I (Sealer+Acid) test specimens were 839 psi at 24 hours, 956 psi at 30 days, and 842 psi at six months. The data for the 24-hour-Group I (Acid+Sealer) test specimens subjected to thermal cycling were comparable to the data obtained for the 24-hour-Group I test specimens not subjected to thermal cycling. A slight decrease of the average bond strengths was noted for the 30-day and six-month-Group I (Acid+Sealer) series of test specimens subjected to thermal cycling when compared to comparable specimens not subjected to thermal cycling. This decrease was not significant at P=0.05 level. The types of bond failure observed for both Group I and II test specimens were mostly adhesive-cohesive separations with a few cohesive failures observed.

Mechanical Stress

The results of intermittent mechanical tensile stressing for Groups I, II, III, and IV immediately after 24 hours, 30 days and six months storage in water appear in Tables VII, VIII, and IX and are summarized in Figures 7, 8, and 9.

The test specimens in control Group IV (untreated enamel surfaces) separated during their respective storage

periods and therefore could not be subjected to the mechanical stress cycling.

None of the test specimens in Group III (Sealer) survived the first stress cycle at a pre-set load value of 300 psi. This would be expected since the average bond strengths for the Group III (Sealer) series of test specimens stored in water were in this range. The types of bond failures observed for specimens in Groups III (Sealer) and IV (Control) indicated that the resin had separated cleanly from the enamel surface.

It can be seen in Tables VII and IX that most of the test specimens in Group II (Acid) survived the 60 stress cycles after storage in water for 24 hours and six months. However, five out of the 10 specimens in the 30-day-Group II (Acid) series failed during stress cycling. The average bond strengths were 651 psi at 24 hours, 446 psi at 30 days, and 523 psi at six months. These values were not statistically different from those obtained for specimens not subjected to mechanical stress cycling. (See Table XVI)

When the phosphoric acid-etched enamel surface was pretreated with the cavity sealer (Group I) the average bond strengths were 746 psi at 24 hours, 862 psi at one month, and 1029 psi at six months. The average mean values were comparable to the data obtained for this Group I (Acid+Sealer) when stored in water. (Tables IV, V, and VI)

There was no significant difference between Groups I and II when stored in water for 24 hours and 30 days and subjected to stress cycling. However, a significant difference (P=0.05) was observed between the six-month-Group I (Acid+Sealer) test specimens and the six-month-Group II (Acid) test specimens subjected to mechanical stress cycling as shown in Table XVI. Examination of each individual tooth surface revealed that the acrylic resin did not separate cleanly from the acid-etched enamel surface for test specimens in both Groups I and II. Varying amounts of acrylic residue were observed.

Temperature and Mechanical Stress

The results of subjecting specimens in Group I (Acid+Sealer) to both temperature and intermittent tensile stress cycling after storage in water for 24 hours, 30 days, and six months, are presented in Table X and are summarized in Figures 7, 8, and 9.

The data showed that the bond strength of the acrylic resin to acid-conditioned enamel surface pretreated with the cavity sealer was unaffected by a combination of thermal and mechanical stress cycling after prolonged storage in water. The average bond strength values were 866 psi at 24 hours, 908 psi at one month, and 787 psi at six months. All of the specimens survived the 60 stress cycles except for one of the six-month test specimens

which separated after six cycles. Examination of the test specimens revealed both adhesive-cohesive and cohesive bond failures.

Part II - Marginal Leakage of Direct Filling Resin

The results obtained from observation of the auto-radiographs using radioactive calcium (Ca^{45}) to assess the marginal seal of a direct filling resin for a limited number of acid-etched Class V preparations are shown in Figures 10 and 11. Three films were selected as being representative for each group and testing condition.

One Week Storage in Water

The control restorations stored in distilled water at 37°C for one week exhibited a slight isotope penetration around the margins of the restorations as shown in Figure 10.

After one-week storage in water, the restorations in which the cavity preparations were etched with 50 per cent phosphoric acid for 60 seconds before placement of the acrylic resin showed virtually no leakage of the radio-isotope as shown in Figure 10.

Thermal Stress

The control restorations subjected to 2500 temperature cycles at a 40°C temperature differential exhibited penetration of the isotope solution across both the gingival and occlusal floors of the cavity preparations in many of the specimens as shown in Figure 11.

The acid-etched resin restorations subjected to the same number of temperature cycles exhibited slightly less isotope leakage than the control restorations, as shown in Figure 11.

Part III - Adhesion of Polycarboxylate Cement

The data for the commercial polycarboxylate cement were not subjected to statistical analysis because of the inconsistent results obtained for both the acid-etched group and control group.

Storage in Water

The results of adhesion tests conducted on the polycarboxylate cement test specimens stored in water for 24 hours, 30 days, and six months are presented in Table XI and are summarized in Figures 12, 13, and 14.

The average bond strength of the cement in the control group stored in water for 24 hours was 41 psi. Pretreatment of the enamel surface with the phosphoric acid improved the average bond strength of the cement to 251 psi. The type of bond failure observed with the acid-etched specimens occurred within the material.

Thirty-day storage in water provided conflicting results. The average bond strength for the control group was 233 psi as compared to 171 psi for the acid-etched group.

Six-month storage in water did not reduce the bond strength of either the control or acid-etched test specimens.

The average bond strength value for the acid-etched specimens was 271 psi as compared to 205 psi for the six-month-control specimens. The data were comparable with data obtained for the 24-hour-acid-etched specimens. All of the bond failures observed with the acid-etched specimens were cohesive. The types of bond failure observed with the control specimens were mostly adhesive-cohesive with varying amounts of cement residue observed on each specimen.

Temperature Stress

The results of tests conducted on acid-etched and non-etched test specimens subjected to thermal stress cycling following 24 hours, 30 days and six months storage in water are presented in Table XII and are summarized in Figures 12, 13, and 14.

The average bond strength for the 24-hour-control group was 163 psi. Pretreatment of the enamel surface with the phosphoric acid slightly improved the bond strength of the cement to 194 psi.

Table XII showed that the adhesive value for the 30-day-acid-etched group was 254 psi as compared to 130 psi for the 30-day-control specimens.

The average bond strength for the six-month-acid-etched specimens was considerably higher than for the six-month-control specimens. The mean value for the acid-etched group was 165 psi as compared to only 17 psi for the control

group. However, the average bond strength for the six-month-acid-etched test specimens was lower than for the 30-day-acid-etched test specimens subjected to thermal stress cycling. Many of the six-month-control specimens separated during the thermal cycling procedure. The types of bond failure observed with the control specimens were both adhesive and adhesive-cohesive separations while the acid-etched specimens exhibited both adhesive-cohesive and cohesive bond failures.

Mechanical Stress

The results of tests conducted on the acid-etched and non-acid-etched test specimens subjected to intermittent tensile stressing at 100 psi for 60 cycles after 24 hours, 30 days, and six months storage in water appear in Tables XIII, XIV, and XV and are summarized in Figures 12, 13, and 14.

All of the 24-hour-control specimens separated before they could be subjected to mechanical stress cycling. The acid-etched specimens exhibited a bond strength of 214 psi. All but three of the 24-hour-acid-etched specimens survived the stress cycling. The types of bond failures observed were both cohesive and adhesive-cohesive for the acid-etched specimens.

The average bond strength obtained for the control specimens stored in water for 30 days was 163 psi as compared

to the bond strength of 128 psi obtained for the acid-etched group. Although the average value was higher for the control test specimens than for the acid-etched test specimens, the latter group exhibited all cohesive breaks with the exception of two specimens.

The average bond strength for the acid-etched test specimens stored in water for six months was 245 psi. This was considerably higher than the average bond strength of 60 psi obtained for the control group test specimens. All of the acid-etched specimens survived the stress cycling with the exception of two specimens. The types of bond failure observed occurred mostly within the cement itself.

TABLES AND FIGURES

TABLE I

Adhesion of Direct Filling Resin to Enamel

24 Hours in H_2O - 37° C**

Spec. No.	Group I (Acid + Sealer)		Group II (Acid)		Group III (Sealer)		Group IV (Control)	
	(psi)	(Type of)* (Break)	(psi)	(Type of)* (Break)	(psi)	(Type of)* (Break)	(psi)	(Type of)* (Break)
1	-	-	601	A-C	364	A-C	58	A
2	1128	A-C	337	A-C	262	A-C	0	A
3	764	C	382	A-C	393	A-C	200	A
4	828	C	501	A-C	641	A-C	0	A
5	983	C	473	A-C	551	A-C	220	A
6	737	C	510	A-C	184	A	121	A
7	910	C	437	A-C	428	A-C	0	A
8	1019	A-C	510	A-C	369	A-C	0	A
9	874	C	364	A-C	352	A-C	0	A
10	992	C	546	A-C	189	A-C	0	A
11	464	A-C	1010	C	388	A-C	146	A
12	1110	A-C	692	C	395	A-C	0	A
13	738	C	701	A-C	391	A-C	8	A
14	-	-	1010	C	240	A-C	0	A
15	774	A-C	873	A-C	151	A-C	0	A
16	1183	C			462	A-C	173	A
Average	893		581		360		64	
Standard Deviation	194		219		132		97	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

** Cross head speed - 0.030 inches/minute

TABLE II

Adhesion of Direct Filling Resin to Enamel

30 Days in H_2O - 37° C**

Spec. No.	Group I (Acid + Sealer) (psi)	(Type of)* (Break)	Group II (Acid) (psi)	(Type of)* (Break)	Group III (Sealer) (psi)	(Type of)* (Break)	Group IV (Control) (psi)	(Type of)* (Break)
1	1074	A-C	637	A-C	0	A	0	A
2	1274	A-C	473	A-C	237	A	0	A
3	874	A-C	364	A-C	146	A	0	A
4	1547	C	328	A-C	237	A	0	A
5	1037	A-C	328	A-C	109	A-C	0	A
6	1074	A-C	346	A-C	164	A	0	A
7	1183	A-C	455	A-C	164	A	0	A
8	1201	A-C	328	A-C	182	A	0	A
9	874	A-C	582	A-C	200	A	0	A
10	1219	A-C	582	A-C	200	A	0	A
Average	1136		442		164		0	
Standard Deviation	199		121		70		0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Cross head speed - 0.030 inches/minute

TABLE III

Adhesion of Direct Filling Resin to Enamel

6 Months in H_2O - 37° C**

Spec. No.	Group I (Acid + Sealer)		Group II (Acid)		Group III (Sealer)		Group IV (Control)	
	(psi)	(Type of)* (Break)	(psi)	(Type of)* (Break)	(psi)	(Type of)* (Break)	(psi)	(Type of)* (Break)
1	1138	A-C	946	A-C	9	A	0	A
2	1219	A-C	710	A-C	300	A-C	0	A
3	1110	A-C	491	A-C	36	A	0	A
4	683	A-C	801	A-C	282	A-C	0	A
5	1219	C	455	A-C	337	A-C	0	A
6	892	A-C	564	A-C	18	A	0	A
7	1019	A-C	346	A-C	291	A-C	0	A
8	1056	A-C	655	A-C	182	A-C	0	A
9	819	A-C	692	A-C	391	A-C	0	A
10	1147	A-C	637	A-C	218	A-C	0	A
Average	1030		630		210		0	
Standard Deviation	179		175		145		0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Cross head speed - 0.030 inches/minute

TABLE IV

Adhesion of Direct Filling Resin to Enamel

24 Hours in H_2O - 37°C & Temperature Cycling**

Spec. No.	Group I (Acid + Sealer) (psi)	Group I (Type of)* (Break)	Group II (Acid) (psi)	Group II (Type of)* (Break)	Group III (Sealer) (psi)	Group III (Type of)* (Break)	Group IV (Control) (psi)	Group IV (Type of)* (Break)
1	510	A-C	673	A-C	0	A	0	A
2	928	A-C	728	A-C	0	A	0	A
3	874	A-C	874	A-C	0	A	0	A
4	692	A-C	273	A-C	0	A	0	A
5	728	A-C	434	A-C	0	A	0	A
6	673	A-C	619	A-C	0	A	0	A
7	819	A-C	1001	A-C	0	A	0	A
8	983	A-C	182	A-C	0	A	0	A
9	837	A-C	1110	A-C	0	A	0	A
10	1347	A-C	1019	A-C	0	A	0	A
Average	839		691		0		0	
Standard Deviation	226		320		0		0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Temperature Differential - 40°C
500 Cycles - 30 seconds
Cross head speed - 0.030 inches/minute

TABLE V

Adhesion of Direct Filling Resin to Enamel

30 Days in H_2O - 37°C & Temperature Cycling**

Spec. No.	Group I (Acid + Sealer) (psi)	(Type of)* (Break)	Group II (Acid) (psi)	(Type of)* (Break)	Group III (Sealer) (psi)	(Type of)* (Break)	Group IV (Control) (psi)	(Type of)* (Break)
1	1201	A-C	637	A-C	0	A	0	A
2	692	A-C	746	A-C	25	A	0	A
3	965	A-C	437	A-C	0	A	0	A
4	1365	C	764	A-C	0	A	0	A
5	728	A-C	437	A-C	0	A	0	A
6	655	A-C	746	A-C	0	A	0	A
7	874	A-C	601	A-C	4	A	0	A
8	1329	C	328	A-C	25	A	0	A
9	1055	A-C	728	A-C	0	A	0	A
10	693	A-C	528	A-C	-	-	0	A
Average	956		595		6		0	
Standard Deviation	272		156		11		0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Temperature Differential - 40°C
500 Cycles - 30 seconds
Cross head speed - 0.030 inches/minute

TABLE VI

Adhesion of Direct Filling Resin to Enamel

6 Months in H_2O - 37°C & Temperature Cycling**

Spec. No.	Group I (Acid + Sealer) (psi)	(Type of)* (Break)	Group II (Acid) (psi)	(Type of)* (Break)	Group III (Sealer) (psi)	(Type of)* (Break)	Group IV (Control) (psi)	(Type of)* (Break)
1	983	A-C	501	A-C	0	A	0	A
2	764	C	228	A	0	A	0	A
3	1183	C	437	A-C	18	A	0	A
4	1128	A-C	501	A-C	137	A-C	0	A
5	783	A-C	801	A-C	182	A-C	0	A
6	783	A-C	419	A-C	27	A-C	0	A
7	601	A-C	701	A-C	9	A	0	A
8	683	A-C	683	A-C	9	A	0	A
9	728	A-C	528	A-C	137	A-C	0	A
10	783	A-C	673	A-C	18	A	0	A
Average	842		547		54		0	
Standard Deviation	192		169		69		0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Temperature Differential - 40°C
500 Cycles - 30 Seconds
Cross head speed - 0.030 inches/minute

TABLE VII

Adhesion of Direct Filling Resin to Enamel

24 Hours in H_2O - 37°C & Stress Cycling at 300 psi****

Spec. No.	Group I (Acid + Sealer)			Group II (Acid)			Group III (Sealer)			Group IV (Control)		
	(psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	(psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	(psi)	(No. of) (Cycles) **	(Type of) (Break) *	(psi)	(No. of) (Cycles) **	(Type of) (Break) *
1	300	38	A-C	300	29	A-C	0	0	A	0	0	A
2	664	60	A-C	582	60	A-C	0	0	A	9	0	A
3	965	60	A-C	437	60	A-C	0	0	A	0	0	A
4	601	60	A-C	655	60	A-C	0	0	A	0	0	A
5	655	60	A-C	419	60	A-C	0	0	A	0	0	A
6	746	60	A-C	528	60	A-C	0	0	A	0	0	A
7	1056	60	A-C	837	60	A-C	0	0	A	0	0	A
8	1238	60	A-C	1274	60	C	0	0	A	0	0	A
9	601	60	A-C	710	60	A-C	9	0	A	0	0	A
10	637	60	A-C	764	60	A-C	0	0	A	9	0	A
Average	746	58		651	57		1	0		2	0	
Standard Deviation	269	7		275	10		3	0		4	0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

****60 cycles at a rate of 0.50 inches/minute
***Cross head speed - 0.30 inches/minute
**When figure is less than 60, specimen broke at that number during cycling

TABLE VIII

Adhesion of Direct Filling Resin to Enamel

30 Days in H_2O - 37°C & Stress Cycling at 300 psi****

Spec. No.	Group I (Acid + Sealer)			Group II (Acid)			Group III (Sealer)			Group IV (Control)		
	(psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	(psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	(psi)	(No. of) (Cycles) **	(Type of) (Break) *	(psi)	(No. of) (Cycles) **	(Type of) (Break) *
1	910	60	A-C	300	7	A-C	0	0	A	0	0	A
2	1092	60	A-C	300	5	A-C	0	0	A	0	0	A
3	1292	60	A-C	300	20	A-C	0	0	A	0	0	A
4	910	60	A-C	673	60	A-C	0	0	A	0	0	A
5	783	60	A-C	491	60	A-C	0	0	A	0	0	A
6	546	60	A-C	510	60	A-C	0	0	A	0	0	A
7	874	60	A-C	473	60	A-C	0	0	A	0	0	A
8	300	40	A-C	300	30	A-C	0	0	A	0	0	A
9	874	60	A-C	437	30	A-C	0	0	A	0	0	A
10	1074	60	A-C	673	60	A-C	0	0	A	0	0	A
verage	862	58		446	42		0	0		0	0	
tandard eviation	275	6		147	24		0	0		0	0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

****60 cycles at a rate of 0.50 inches/minute
***Cross head speed - 0.030 inches/minute
**When figure is less than 60, specimen broke at that number during cycling

TABLE IX

Adhesion of Direct Filling Resin to Enamel

6 Months in H_2O - 37° C & Stress Cycling at 300 psi****

Spec. No.	Group I (Acid + Sealer)			Group II (Acid)			Group III (Sealer)			Group IV (Control)		
	(psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	(psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	(psi)	(No. of) (Cycles) **	(Type of) (Break) *	(psi)	(No. of) (Cycles) **	(Type of) (Break) *
1	1192	60	A-C	628	60	A-C	255	0	A-C	0	0	A
2	956	60	A-C	473	60	A-C	182	0	A-C	0	0	A
3	956	60	A-C	910	60	A-C	55	0	A	0	0	A
4	1037	60	A-C	300	30	A-C	18	0	A	0	0	A
5	1219	60	A-C	592	60	A-C	9	0	A	0	0	A
6	1147	60	A-C	482	60	A-C	18	0	A	0	0	A
7	1001	60	A-C	300	6	A-C	0	0	A	0	0	A
8	783	60	A-C	655	60	A-C	0	0	A	0	0	A
9	1037	60	A-C	382	60	A-C	0	0	A	0	0	A
10	965	60	A-C	510	60	A-C	0	0	A	0	0	A
verage	1029	60		523	51		54	0		0	0	
tandard eviation	130	0		185	19		90	0		0	0	

* A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

****60 cycles at a rate of 0.50 inches/minute
***Cross head speed - 0.030 inches/minute
**When figure is less than 60, specimen broke at that number during cycling

TABLE X

Adhesion of Direct Filling Resin to Enamel

Storage in H_2O - 37°C, Temperature Cycling**** & Stress Cycling at 300 psi*****

Group I (Acid + Sealer)

Spec. No.	24 Hours			30 Days			6 Months		
	(psi) ++	** (No. of) (Cycles)	*** (Type of) (Break)	(psi) ++	** (No. of) (Cycles)	*** (Type of) (Break)	(psi) ++	** (No. of) (Cycles)	*** (Type of) (Break)
1	764	60	A-C	619	60	A-C	1047	60	C
2	874	60	A-C	1183	60	A-C	810	60	C
3	1074	60	A-C	946	60	A-C	701	60	A-C
4	619	60	A-C	1347	60	A-C	1238	60	A-C
5	910	60	A-C	783	60	A-C	728	60	A-C
6	564	60	A-C	874	60	A-C	300	6	A-C
7	1037	60	C	637	60	A-C	473	60	A-C
8	801	60	A-C	1092	60	A-C	664	60	A-C
9	965	60	A-C	801	60	A-C	1092	60	A-C
10	1056	60	A-C	801	60	A-C	819	60	A-C
Average	866	60		908	60		787	55	
Standard Deviation	179	0		236	0		284	17	

***A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

*****60cycles at a rate of 0.50 inches/minute
****Temperature differential - 40°C
500 cycles - 30 seconds
**When figure is less than 60, specimen broke at that number during cycling
++Cross head speed - 0.030 inches/minute

TABLE XI

Adhesion of Polycarboxylate Cement to Enamel

Storage in H_2O - 37°C **

	24 Hours				30 Days				6 Months			
	Group I (Acid)		Group II (Control)		Group I (Acid)		Group II (Control)		Group I (Acid)		Group II (Control)	
Spec. No.	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)
1	228	C	0	A	182	A-C	0	A	364	C	164	A-C
2	182	C	0	A	127	C	2288	C	209	C	109	C
3	255	A-C	0	A	273	C	237	C	309	C	182	A-C
4	228	A-C	36	A	273	C	282	A-C	218	C	346	A-C
5	291	C	0	A	309	C	182	C	373	C	237	A-C
6	228	C	0	A	309	A-C	300	C	319	C	228	C
7	337	C	109	A	127	C	364	C	282	A-C	173	A-C
8	273	C	0	A	146	C	400	C	346	C	228	A-C
9	255	C	164	A	228	C	146	A-C	146	C	228	A-C
10	228	C	109	A	146	C	191	A-C	146	C	155	A-C
Average	251		41		171		233		271		205	
Standard Deviation	41		61		101		114		86		64	

*A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Cross head speed - 0.030 inches/minute

TABLE XII

Adhesion of Polycarboxylate Cement to Enamel

Storage in H_2O - 37°C & Temperature Cycling **

	24 Hours				30 Days				6 Months			
	Group I (Acid)		Group II (Control)		Group I (Acid)		Group II (Control)		Group I (Acid)		Group II (Control)	
Spec. No.	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)	(psi)	(Type of) (Break)
1	228	C	182	A	237	A-C	118	A-C	146	C	0	A
2	164	A-C	218	C	282	A-C	173	A-C	55	A-C	146	A-C
3	273	C	218	C	182	A	18	A	273	A-C	27	A
4	182	C	127	A	319	C	400	C	73	A-C	0	A
5	182	A-C	146	A	146	C	46	A	146	C	0	A
6	164	C	264	C	437	A-C	264	A-C	209	C	0	A
7	91	C	118	A	300	A-C	0	A	346	C	0	A
8	237	C	36	A	127	A-C	55	A-C	91	A-C	0	A
9	237	C	164	C	218	A-C	191	C	209	A-C	0	A
10	146	A-C	-	-	291	A-C	100	A-C	109	A-C	0	A
Average	194		163		254		138		165		17	
Standard Deviation	58		67		92		122		93		46	

*A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

**Temperature differential - 40°C
500 cycles - 30 seconds
Cross head speed - 0.030 inches/minute

TABLE XIII

Adhesion of Polycarboxylate Cement to Enamel

24 Hours in H_2O - 37°C & Stress Cycling at 100 psi****

Spec. No.	Group I (Acid) (psi)***	(No. of) (Cycles)**	(Type of) (Break)*	Group II (Control) (psi)	(No. of) (Cycles)**	(Type of) (Break)*
1	100	6	A-C	0	0	A
2	300	60	C	0	0	A
3	355	60	C	0	0	A
4	100	18	A-C	0	0	A
5	100	23	C	0	0	A
6	100	60	A-C	0	0	A
7	282	60	C	0	0	A
8	282	60	A-C	0	0	A
9	291	60	C	0	0	A
10	237	60	C			
Average	214	47		0	0	
Standard Deviation	102	21		0	0	

*A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

****60 cycles at a rate of 0.50 inches/minute
***Cross head speed - 0.030 inches/minute
**When figure is less than 60, specimen broke at that number during cycling

TABLE XIV

Adhesion of Polycarboxylate Cement to Enamel

30 Days in H_2O - 37°C & Stress Cycling at 100 psi****

Spec. No.	Group I (Acid) (psi) ***	(No. of) (Cycles) **	(Type of) (Break) *	Group II (Control) (psi) ***	(No. of) (Cycles) **	(Type of) (Break) *
1	100	2	C	100	1	C
2	100	1	C	100	10	A-C
3	100	10	C	273	60	C
4	100	1	C	100	51	C
5	100	1	C	100	25	C
6	100	24	C	100	41	A-C
7	100	3	A	319	60	A-C
8	382	60	C	100	3	A-C
9	100	1	C	100	4	C
10	100	1	C	273	60	C
Average	128	10		163	31	
Standard Deviation	89	19		107	25	

*A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

****60cycles at a rate of 0.50 inches/minute
***Cross head speed - 0.30 inches/minute
**When figure is less than 60, specimen broke at that number during cycling

TABLE XV

Adhesion of Polycarboxylate Cement to Enamel

6 Months in H_2O - 37°C & Stress Cycling at 100 psi****

Spec. No.	Group I (Acid) (psi)	** (No. of) (Cycles)	* (Type of) (Break)	Group II (Control) (psi)	** (No. of) (Cycles)	* (Type of) (Break)
1	328	60	C	0	0	A
2	100	41	C	100	38	A-C
3	291	60	C	100	23	A-C
4	100	23	A-C	0	0	A
5	400	60	C	100	3	A-C
6	300	60	C	100	4	A-C
7	328	60	C	0	0	A
8	273	60	C	100	1	C
9	328	60	A-C	100	3	A-C
10	-	-		0	0	A-C
Average	245	53		60	7	
Standard Deviation	103	13		52	13	

*A=Adhesive
C=Cohesive
A-C=Adhesive & Cohesive

****60 cycles at a rate of 0.50 inches/minute
***Cross head speed - 0.30 inches/minute
**When figure is less than 60, specimen broke at that number during cycling.

TABLE XVI

Comparison among 39 groups of direct filling resin, arranged in descending order according to the magnitude of group means.

Group	Significance under Newman-Keul's Test*	Sample Size	Mean	Standard Deviation
I - 30 Days - H_2O		10	1136	199
I - 6 Months - H_2O		10	1030	179
I - 6 Months - S.C.		10	1029	130
I - 30 Days - T.C.		10	956	272
I - 30 Days - T.C. & S.C.		10	908	236
I - 24 Hours - H_2O		14	893	194
I - 24 Hours - T.C. & S.C.		10	866	179
I - 30 Days - S.C.		10	862	275
I - 6 Months - T.C.		10	842	192
I - 24 Hours - T.C.		10	839	226
I - 6 Months - T.C. & S.C.		10	787	284
I - 24 Hours - S.C.		10	746	270
II - 24 Hours - T.C.		10	691	320
II - 24 Hours - S.C.		10	651	275
II - 6 Months - H_2O		10	630	175
II - 30 Days - T.C.		16	595	156
II - 24 Hours - H_2O		10	581	219
II - 6 Months - T.C.		10	547	169
II - 6 Months - S.C.		10	523	185
II - 30 Days - S.C.		10	446	147
II - 30 Days - H_2O		10	442	121
III - 24 Hours - H_2O		16	360	132
III - 6 Months - H_2O		10	210	145
III - 30 Days - H_2O		10	164	70
IV - 24 Hours - H_2O		16	64	97
III - 6 Months - T.C.		10	54	69
III - 6 Months - S.C.		10	54	90
III - 30 Days - T.C.		9	6	11
IV - 24 Hours - S.C.		10	2	4
III - 24 Hours - S.C.		10	1	3
IV - 24 Hours - T.C.		10	0	0
III - 24 Hours - T.C.		10	0	0
IV - 30 Days - T.C.		10	0	0
IV - 30 Days - H_2O		10	0	0
IV - 30 Days - S.C.		10	0	0
III - 30 Days - S.C.		10	0	0
IV - 6 Months - T.C.		10	0	0
IV - 6 Months - H_2O		10	0	0
IV - 6 Months - S.C.		8	0	0

-continued-

TABLE XVI

(cont.)

* Groups included within the same line are not significantly different from each other at the 0.05 probability level; and those groups not included within the same line are significantly different from each other.

T.C. - Temperature stress cycling

S.C. - Intermittent stress cycling

TABLE XVII

Group	Sample Size	Mean	Standard Deviation
I - 6 Months - H_2O	10	271	86
I - 30 Days - T.C.	10	254	92
I - 24 Hours - H_2O	10	251	41
I - 6 Months - S.C.	9	245	103
II - 30 Days - H_2O	10	233	114
I - 24 Hours - S.C.	10	214	102
II - 6 Months - H_2O	10	205	86
I - 24 Hours - T.C.	10	194	58
I - 30 Days - H_2O	10	171	101
I - 6 Months - T.C.	10	165	93
II - 24 Hours - T.C.	9	163	67
II - 30 Days - S.C.	10	163	107
II - 30 Days - T.C.	10	138	122
I - 30 Days - S.C.	10	128	89
II - 6 Months - S.C.	10	60	52
II - 24 Hours - H_2O	10	41	61
II - 6 Months - T.C.	10	17	46
II - 24 Hours - S.C.	10	0	0

I = Acid-etched group

II = Control group

T.C. - Temperature stress cycling

S.C. - Intermittent stress cycling

Figure 1. Bovine tooth prepared for mounting and specimen mounted in acrylic resin

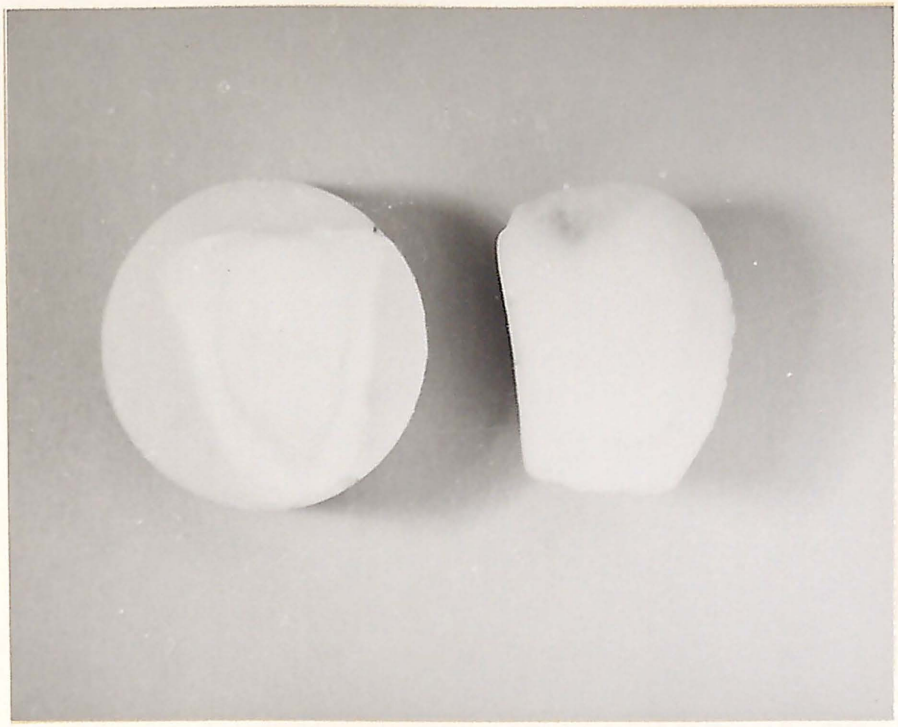


Figure 2. Photograph of mounted test specimen.

Figure 3. Cross section of adhesion test specimen

A. Brass ball bearing.
B. Adhesive.
C. Excess adhesive.
D. Silicon matrix.
E. Brass ring for stabilizing matrix.
F. Bovine tooth.

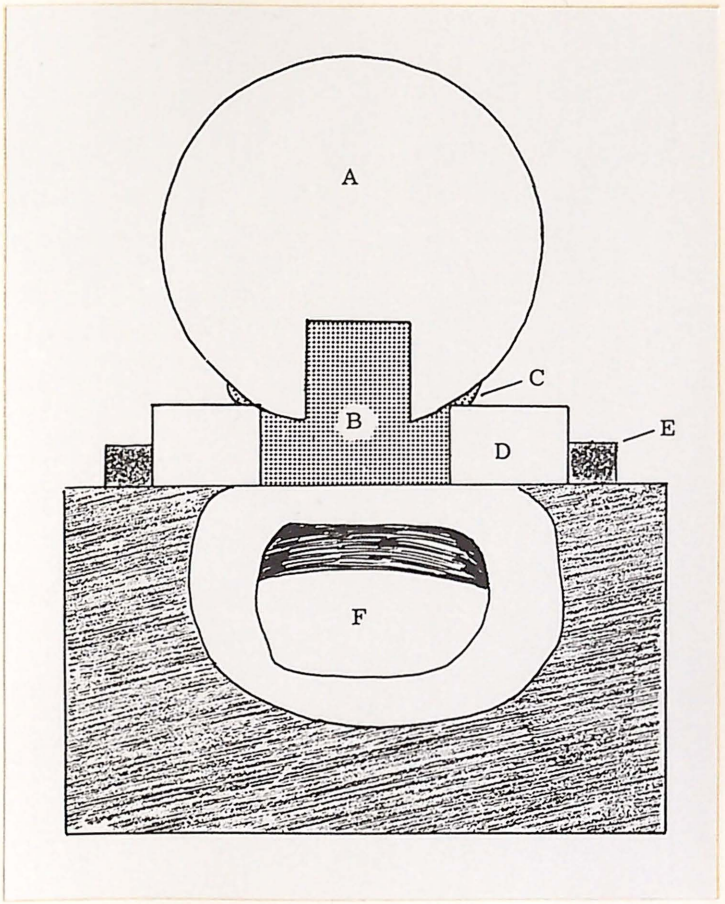

A
B
C
D
E
F

Figure 4. Diagram of adhesion testing apparatus for mounting into testing machine. A. Brass ring; B. Brass support plate pivoted off of brass ring; C. Support plate pivoted off support plate B; D. Test specimen; E. Slotted brass tube to serve as attachment of specimen in tensile grips; F. Wires for attachment in grips of tensile test machine. All joints are freely movable to permit proper alignment of specimen during testing.

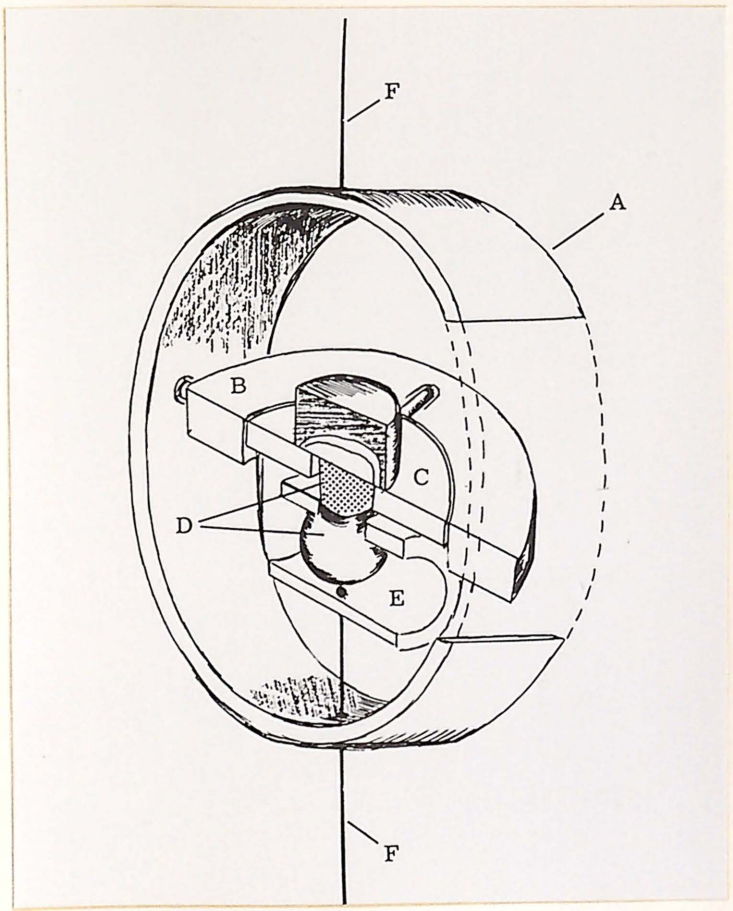

F
A
B
C
D
E
F

Figure 5. Temperature cycling apparatus. The specimens were placed in the wire mesh container and cycled between the two water baths. The temperature differential was controlled by the water circulating through the metal tanks. The automatic timer and counting device can be seen on the control panel to the right.

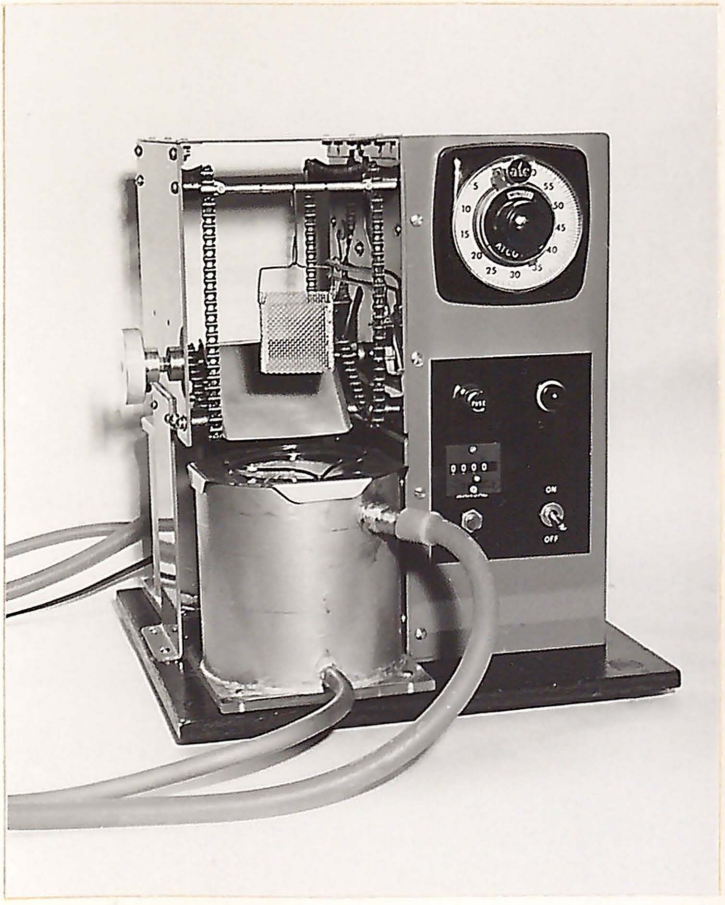
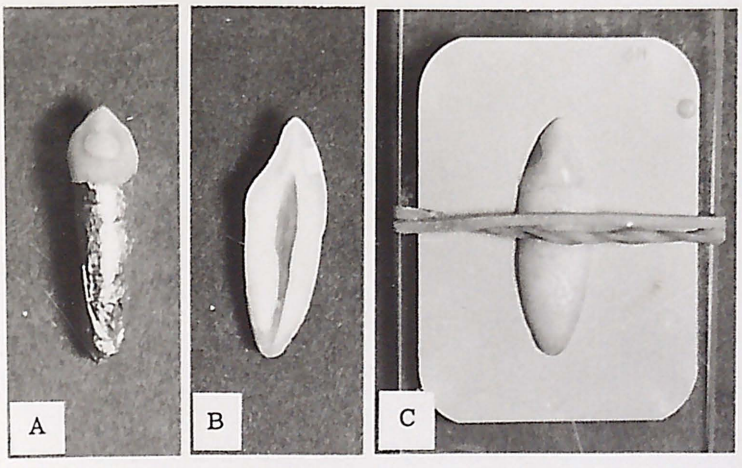

ON
OFF

Figure 6. Preparation of tooth for isotope test and autoradiographs.

A. Tooth sealed with tin foil for immersion in isotope.

B. Tooth sectioned through restoration for placement on film.

C. Tooth mounted on film.



Sealed Sectioned On Film

FIG. 3

Figure 7. Summary of 24-hour data on the adhesion of direct filling resin.

DIRECT FILLING RESIN
24 HRS. DISTILLED H_2O - 37^{O} C

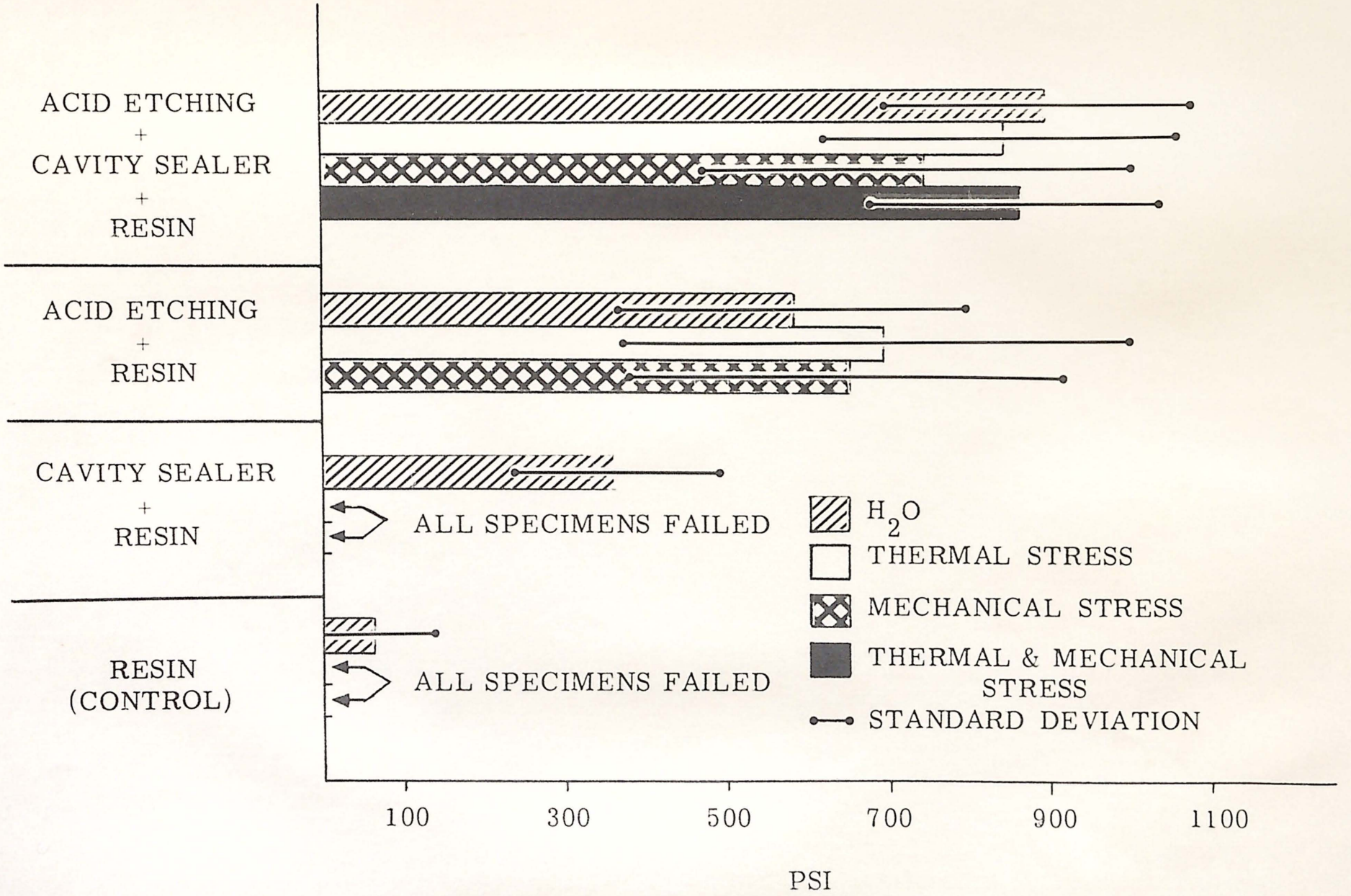


Figure 8. Summary of 30-day data on the adhesion of direct filling resin.

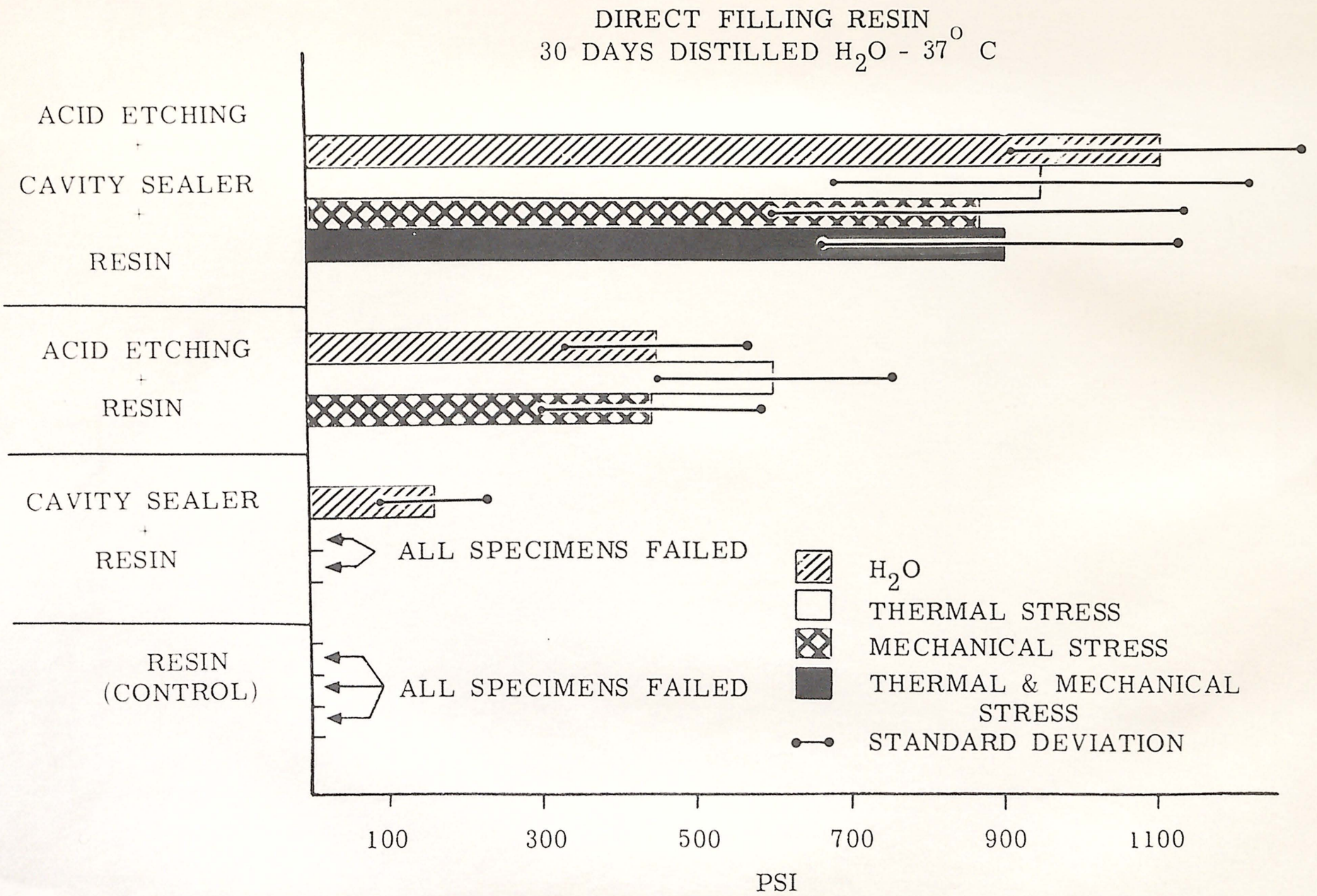

DIRECT FILLING RESIN
30 DAYS DISTILLED H_2O - 37° C
ACID ETCHING + CAVITY SEALER + RESIN
ACID ETCHING + RESIN
CAVITY SEALER + RESIN
RESIN (CONTROL)
ALL SPECIMENS FAILED
ALL SPECIMENS FAILED
H_2O
THERMAL STRESS
MECHANICAL STRESS
THERMAL & MECHANICAL STRESS
STANDARD DEVIATION
100
300
500
700
900
1100
PSI

Figure 9. Summary of 6-month data on the adhesion of direct filling resin.

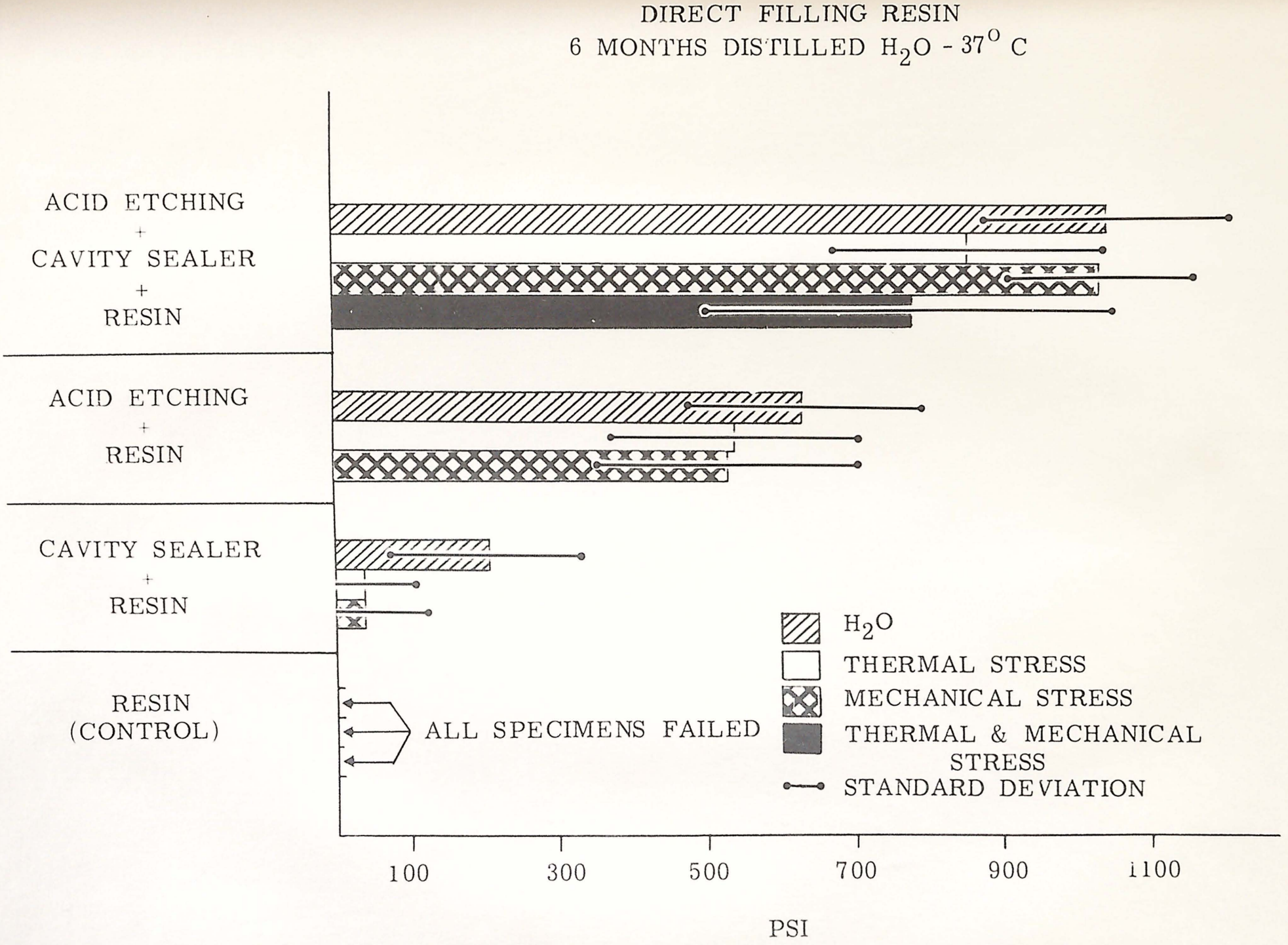

DIRECT FILLING RESIN
6 MONTHS DISTILLED H_2O - 37° C
ACID ETCHING
+
CAVITY SEALER
+
RESIN
ACID ETCHING
+
RESIN
CAVITY SEALER
+
RESIN
RESIN
(CONTROL)
ALL SPECIMENS FAILED
H_2O
THERMAL STRESS
MECHANICAL STRESS
THERMAL & MECHANICAL STRESS
STANDARD DEVIATION
100
300
500
700
900
1100
PSI

Figure 10. Autoradiographs of acid-etched and non-etched teeth restored with direct filling resin after one-week storage in water at 37°C.

ONE WEEK STORAGE IN DISTILLED H_2O - 37^oC

ACID - ETCHED PREPARATIONS

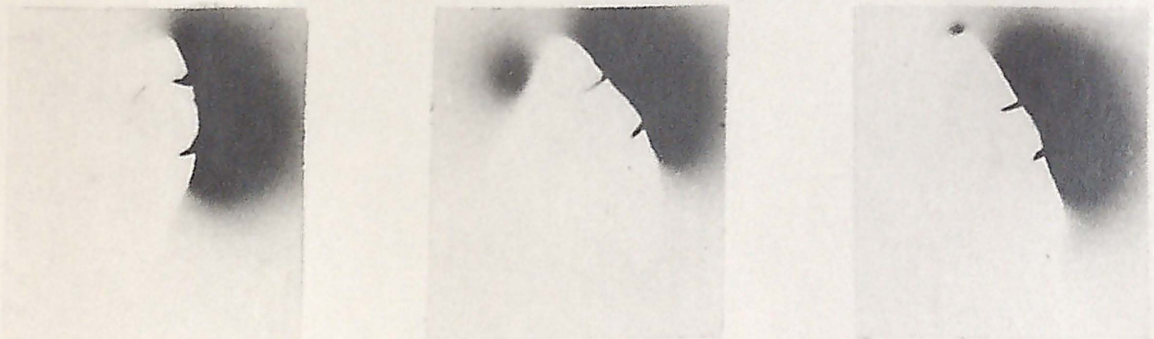
CONTROL PREPARATIONS

DIRECT FILLING RESIN

Figure 11. Autoradiographs of acid-etched and non-etched teeth restored with direct filling resin after being subjected to 2500 temperature cycles at a 40°C temperature differential and 30 second immersion time in each bath.

2500 TEMPERATURE CYCLES

ACID - ETCHED PREPARATIONS



CONTROL PREPARATIONS

DIRECT FILLING RESIN

Figure 12. Summary of 24-hour data on the adhesion of polycarboxylate cement.

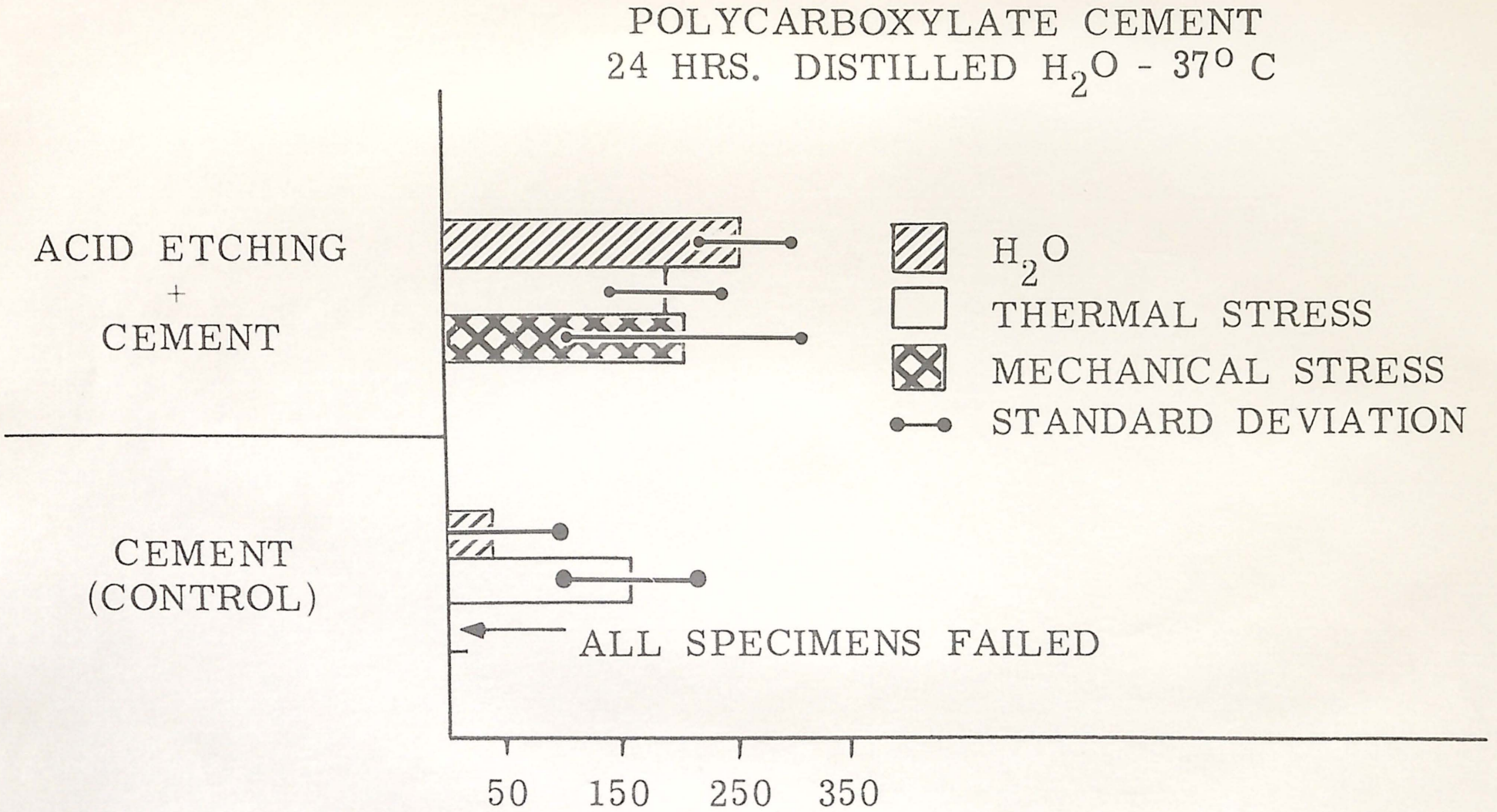

POLYCARBOXYLATE CEMENT
24 HRS. DISTILLED H_2O - 37° C
ACID ETCHING
+
CEMENT
CEMENT
(CONTROL)
H_2O
THERMAL STRESS
MECHANICAL STRESS
STANDARD DEVIATION
ALL SPECIMENS FAILED
50
150
250
350

Figure 13. Summary of 30-day data on the adhesion of polycarboxylate cement.

POLYCARBOXYLATE CEMENT
30 DAYS DISTILLED H_2O _ 37^{O} C

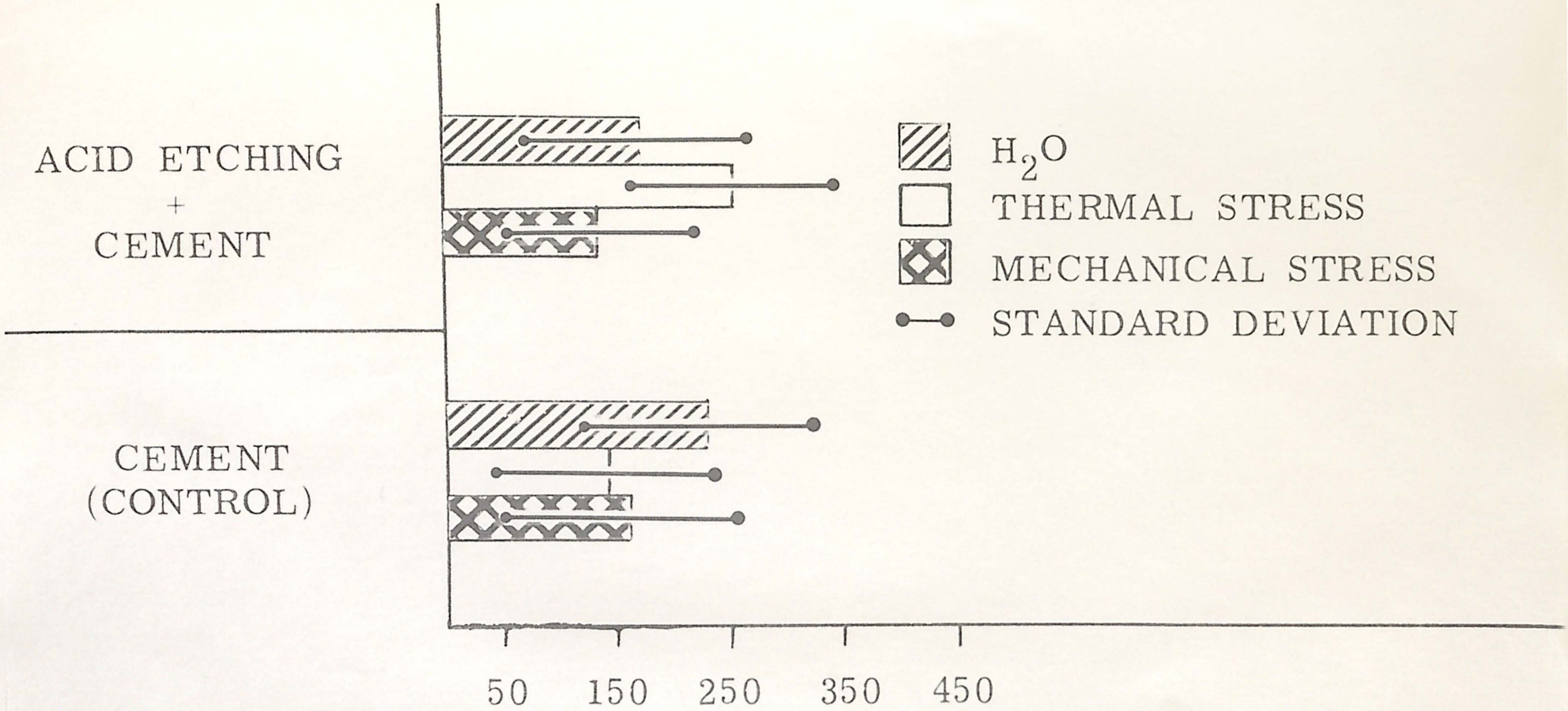
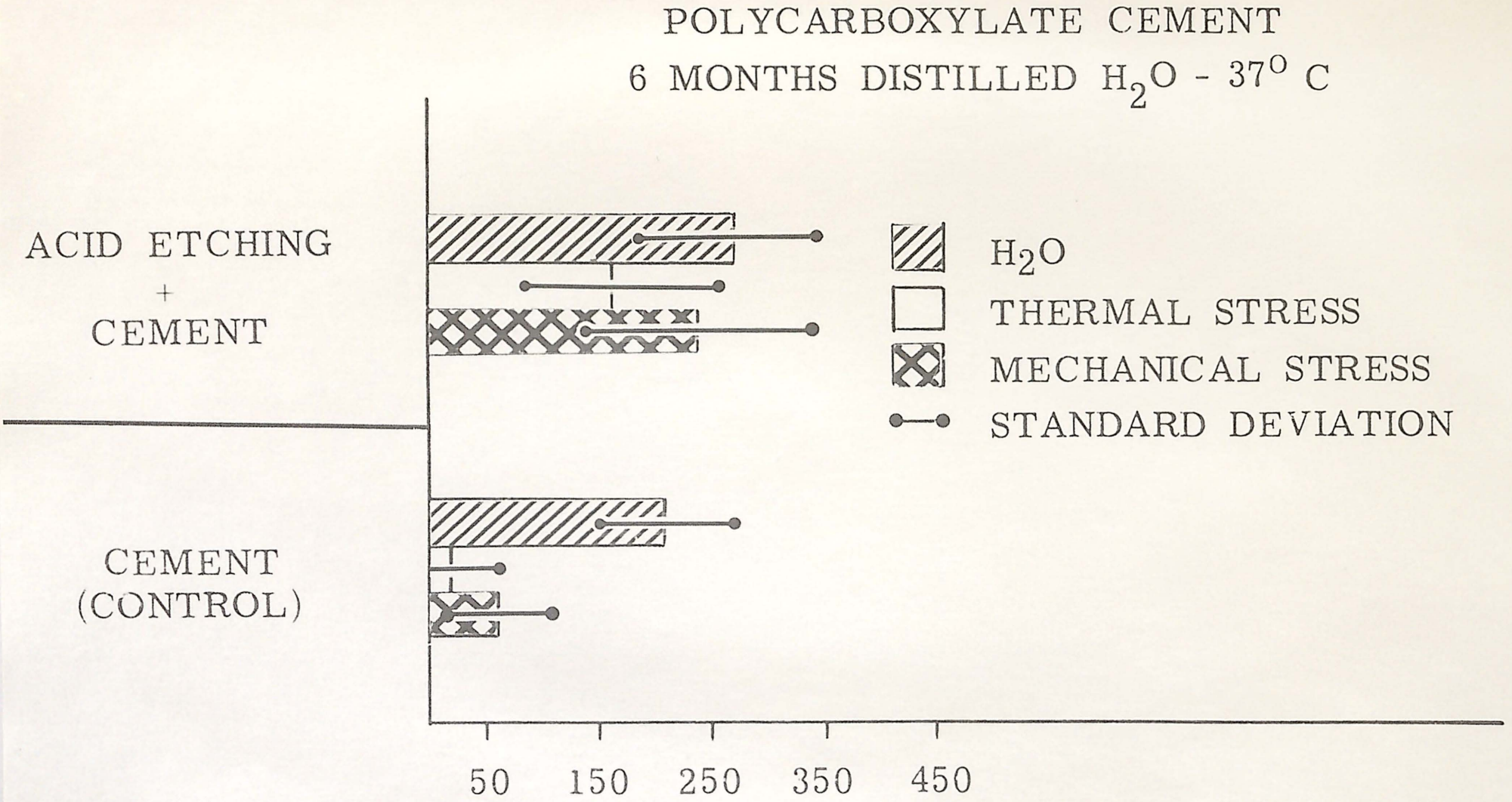


Figure 14. Summary of 6-month data on the adhesion of polycarboxylate cement.


POLYCARBOXYLATE CEMENT
6 MONTHS DISTILLED H_2O - 37^O C
ACID ETCHING
+
CEMENT
CEMENT
(CONTROL)
H_2O
THERMAL STRESS
MECHANICAL STRESS
STANDARD DEVIATION
50
150
250
350
450

DISCUSSION

Part I

Adhesion of Direct Filling Resin

The primary objective of this study was to determine whether etching of the enamel surface with 50 per cent phosphoric acid would increase the bonding of a commercial restorative acrylic resin. The results indicate that a 50 per cent aqueous solution of phosphoric acid when applied to bovine enamel for 60 seconds significantly ($P=0.05$) increases the bonding of the restorative acrylic resin and that the cavity sealer supplied by the manufacturer further enhances the bonding of the acrylic resin when applied on an enamel surface pretreated with phosphoric acid.

The results of this study agree with the findings of other investigators[3,8,9,10,12,14,38,51,54,55,56,59,113,114] who also have reported increased bonding of resin materials to tooth structure pretreated with organic or inorganic acids.

Table XVI shows that the highest average values were obtained with the Group I series of test specimens in which the cavity sealer was applied to bovine enamel surface

preconditioned with the phosphoric acid. The next highest values were obtained with the Group II series of specimens in which the enamel surface was preconditioned with only the phosphoric acid before applying the acrylic resin. The Newman-Keul's test (Table XVI) indicates that under conditions of prolonged storage in water, and temperature and intermittent tensile stressing, the acrylic resin attachment to the acid-etched enamel surface is unaffected for test specimens in both Groups I and II. Even when the Group I series of specimens were subjected to both temperature and intermittent tensile stress cycling after prolonged storage in water, the bonding of the acrylic resin to the acid-etched enamel surface was unaffected.

Although the average bond strength values were consistently higher for the Group I specimens (Acid+Sealer) than for the Group II (Acid) test specimens, the statistical difference between the two groups which had been subjected to the same storage times and testing conditions was not great. The Newman-Keul's test revealed that the only significant difference between test specimens in Groups I and II at $P=0.05$ level was found in the specimens stored in water for one month and six months, and for the six-month specimens stored in water and then subjected to intermittent tensile stressing as shown in Table XVI.

The enhanced bonding of the acrylic resin achieved by pretreating the enamel surface with 50 per cent phosphoric acid may have been the result of the acid (1) "exposing the organic framework of enamel which served as a network in and about which the acrylic might mechanically adhere to" or (2) "removing the old, fully reacted inert enamel surface and then exposing a fresh reactive surface more favorable to adhesion" as postulated by Buonocore.[38] The acid may have increased the surface area and wettability of the tooth surface thus achieving the molecular closeness necessary for maintaining adhesion.[9,59,64,113]

The data obtained from this study confirm neither "adhesion" or "mechanical retention" as the means by which acid-etching of enamel surfaces improves the bonding of acrylic resin. However, since "adhesion" of acrylic resin on unaltered tooth structure is readily destroyed by water or moisture, as shown by this study and by other investigators,[37,39,48,69,71] the enhanced bonding of the acrylic resin to acid-conditioned enamel surfaces is probably related more to mechanical retention than to adhesion alone.

In this study the resin attachment to acid-conditioned enamel surfaces appeared to be unaffected by prolonged storage in water. This finding is also reported by Laswell, Welk, and Regenos.[3]

The electron microradiographs shown by Sharp[111] and Poole and Johnson[112] revealed a honeycomb structure of the enamel surface following etching with various acids. This honeycomb framework may have provided the means by which the acrylic resin was able to mechanically attach to the tooth surface. The findings of Gwinnett,[58] Matsui,[55] and Buonocore,[57] confirmed filamentous "tag-like" extensions 15-20 microns long, which were seen at the interface where the resin material contacted the etched-enamel surface, suggesting the possibility of mechanical retention.

The improved bonding of the acrylic resin achieved when the cavity sealer was used on the acid-etched enamel surfaces may be related to its low surface tension, which allows it to flow more readily into the surface irregularities of the tooth surface. In addition, the cavity sealer may have contributed to the cleaning of the tooth surface, as suggested by Swartz,[74] so that better wetting of the acrylic resin could take place. Other studies[42,52,69,103,105] have reported that this same cavity sealer improved the adhesion and sealing property of a commercial direct filling resin on untreated enamel and dentin surfaces.

In this study the cavity sealer significantly improved the adhesion of the acrylic resin to a polished enamel surface, even after 24 hours storage in water, as shown in Table XVI for the Group III series of test specimens.

However adhesion was significantly reduced when the Group III (Sealer) series of test specimens was subjected to longer storage periods in water and to temperature and intermittent tensile stressing. Without some form of mechanical retention, moisture, thermal and mechanical stress either reduced or destroyed the adhesion of the acrylic resin on polished enamel surfaces treated with or without the cavity sealer.

Examination of each specimen in Groups I and II under a dissecting microscope at 20 power revealed that the acrylic resin either fractured partially (adhesive-cohesive) or wholly (cohesive) within the material, indicating that the bond strength of the acrylic resin to acid-etched enamel surfaces exceeded the tensile strength of the resin material.

The results of this study support the view of Doyle[2] and others[3] that the "Etched Restoration Technique" for restoring small incisal fractures and hypoplastic defects in anterior permanent teeth may be indicated as a method for securing resin attachment to tooth structure without having to utilize pins or undercuts in the preparation for achieving mechanical retention. Although the laboratory testing conditions of prolonged storage in water, temperature stressing, and intermittent tensile stressing to which the acid-etched specimens were subjected parallels some of the

conditions found within the oral environment, they do not provide information as to whether this improved bonding of a conventional unfilled restorative resin to acid-etched tooth surfaces will be maintained in the oral cavity over long periods. Therefore, further laboratory testing followed by a long-termed clinical study is needed to substantiate the laboratory findings of this investigation.

Part II

Marginal Leakage of Direct Filling Resin

Improvement in the marginal seal of a conventional restorative acrylic resin was observed after one-week storage in water when the cavity preparation was etched with a 50 per cent solution of phosphoric acid for 60 seconds as compared to the non-etched control restorations. The improvement in marginal seal of the restorative material to the acid-etched cavity preparation may have been related to the removal by the acid of the surface debris produced during cavity instrumentation,[72,73] or to the acid's conversion of a normally low energy surface to a more wettable high energy surface which allows for closer adaptation of the resin material to the cavity walls of the preparation.[9,64,69,113]

However, a substantial increase in isotope penetration was observed for both the acid-etched and non-etched resin restorations when they were subjected to 2500 thermal stress cycles. This increase in marginal leakage may have been

related to the high thermal coefficient of expansion inherent in conventional unfilled restorative resin materials.[21,26,31] The stress induced during the prolonged thermal stressing may have been great enough to separate the resin from the acid-etched tooth surface. Whether this separation occurred at the resin-tooth-interface or within the material of the acid-etched restorations cannot be determined from this part of the study.

Part III

Adhesion of the Polycarboxylate Cement

The data for the polycarboxylate cement specimens were not subjected to a statistical analysis because some of the values obtained for the acid-etched and control groups did not provide a true comparison of the bond strength of the cement to the tooth surface.

The average mean values as shown in Table XVII were consistently higher for the acid-etched group than for the control group. In two instances the average mean value for the control group was higher than for the acid-etched group, as shown in Tables XI and XIV. However, the data obtained for the acid-etched group do not provide a true indication of the bond strength of the cement to the tooth surface because most of the failures occurred within the cement itself. These results indicate that the bond strength of the cement

to the acid-conditioned enamel surface exceeded the tensile strength of the material. Careful examination of the fractured area revealed the incorporation of air bubbles within the cement, which could have contributed to a reduction in the tensile strength of the material.

The results of this study indicate that prolonged storage in water, temperature stress cycling and intermittent tensile stress cycling do not affect the bonding of the polycarboxylate cement to acid-etched enamel surfaces. The acid-etched specimens exhibited more cohesive failures than the control group.

The data obtained for the control group test specimens provided inconsistent and conflicting results. Twenty-four hours storage in water appeared to have affected the adhesion of the cement to the polished enamel surface but did not affect the adhesion of the same group of specimens when stored in water for 30 days and for six months, as shown in Table XI. Furthermore, this inconsistency was also observed with the data obtained for the control specimens subjected to intermittent stress cycling after storage in water for 24 hours, 30 days, and six months. The 30-day results were higher than the 24-hour and six-month results, as shown in Figures 12, 13, and 14. These conflicting results may have been attributed to the incorporation of air bubbles during mixing of the cement, to

microscopic debris on the tooth surface which prevented proper wetting of the cement to that surface, to variations in the surface energy of the tooth surface for each individual specimen, or to the tensile test method.

Similar variations in the data were also observed for the acid-etched group subjected to storage in water, and thermal and mechanical stress cycling.

The adhesion values obtained for the control specimens support the findings of Smith,[47] and Swartz, Phillips, and Norman,[97] and Mizrahi and Smith.[100] The consistently higher average bond strengths obtained for the phosphoric-acid-etched specimens do not agree with the findings of Mizrahi and Smith,[100] who reported that etching of the enamel surface with phosphoric acid did not increase the adhesion of the polycarboxylate cement. However, they used only a one per cent solution of phosphoric acid which was left on for five minutes.

One would not expect acid-etching of the tooth surface to enhance the bonding of this material since its "adhesive" property depends upon a very close contact with the tooth surface void of any surface irregularities. Etching of the enamel surface with phosphoric acid produces a rough surface which would prevent the cement from achieving molecular closeness necessary for maintaining adhesion. However, the

improved adhesion of the polycarboxylate cement on acid-etched enamel surfaces suggests the possibilities that the acid may have contributed to the cleaning of the tooth surface by removing organic debris to improve wetting,[72,73,113] or to the converting of a normally hydrophobic, low energy tooth surface to a more hydrophilic high energy surface ready to accept a low energy adhesive material.[9,39]

Further study in the laboratory with different acids at varying concentrations and varying lengths of time left on the tooth surface will be needed to substantiate the findings of this part of the investigation.

SUMMARY AND CONCLUSIONS

The primary purpose of this laboratory study was to determine whether the bonding of a conventional unfilled restorative acrylic resin to bovine enamel surfaces is increased by the pretreatment of the enamel surface with a 50 per cent aqueous solution of phosphoric acid for 60 seconds. A tensile test was used to measure the bond strength of the acrylic resin to the tooth surface.

A total of 414 bovine teeth were divided into four principal groups: In Group I the enamel surface was pretreated with the phosphoric acid and the cavity sealer supplied by the manufacturer. In Group II the enamel surface was pretreated with phosphoric acid. In Group III the enamel surface was pretreated with the cavity sealer; and in Group IV the enamel surface was left untreated. The latter group served as the control. The four groups were subjected to storage in water for 24 hours, 30 days, and six months. The effects of temperature cycling and intermittent tensile stress cycling on the strength of the bond also were investigated.

The results indicate that pretreating the enamel surface with the 50 per cent phosphoric acid for 60 seconds significantly increased the bonding of the restorative resin, and that the use of the cavity sealer in conjunction

with acid etching further enhanced the attachment of the resin to enamel surface.

Under the conditions of this study, attachment of the acrylic resin to the acid-conditioned enamel surface was unaffected by prolonged storage in water, by temperature cycling, and by intermittent tensile stress cycling. The statistical difference between the bond strengths of Group I and Group II was small.

Prolonged storage in water, temperature cycling, and mechanical stress cycling produced a significant reduction in the adhesion of the acrylic resin to polished enamel surfaces for both Groups III and IV when the cavity sealer was used and when it was not employed.

Most of the bond failures observed with the acid-etched specimens in Groups I and II were either cohesive or adhesive-cohesive, indicating that the bond strength of the resin exceeded the material's inherent tensile strength.

A limited number of resin restorations were placed into Class V preparations etched with 50 per cent phosphoric acid for 60 seconds, and radioactive calcium (Ca^{45}) was used to assess the marginal seal. The autoradiographs showed that etching of Class V preparations with phosphoric acid appeared to improve the marginal seal of the acrylic resin after one-week storage in water. However, only a slight improvement in the marginal seal of acid-etched

restorations was observed when compared to the control restorations when both were subjected to 2500 thermal stress cycles at a 40°C temperature differential.

The adhesion of a new polycarboxylate cement to bovine enamel pretreated with and without 50 per cent phosphoric acid was also measured employing the same test conditions and method of testing as were used on the restorative acrylic resin specimens.

One hundred and eighty specimens were divided into two groups. In Group I the enamel surface was pretreated with 50 per cent phosphoric acid for 60 seconds. Group II served as the control specimens.

The data revealed that etching of the enamel surface provided slightly higher adhesive values than in the control group. In two instances in which the mean values for the control group were higher than for the acid-etched group, the bond failures of the acid-etched group occurred within the material and not at the resin-tooth-interface. This type of bond failure does not allow for a true comparison of the bond strengths between the two groups.

Results showed that prolonged storage in water, thermal stressing, and intermittent tensile stressing did not affect the adhesion of the cement to acid-etched enamel surfaces. However, thermal cycling after six-month storage in water and intermittent stress cycling after prolonged storage in water appeared to decrease the adhesion of the polycarboxylate cement to polished enamel surfaces.

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CURRICULUM VITAE

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ABSTRACT

A LABORATORY STUDY OF THE ADHESION OF A RESTORATIVE ACRYLIC RESIN AND A POLYCARBOXYLATE CEMENT ON BOVINE ENAMEL ETCHED WITH FIFTY PER CENT PHOSPHORIC ACID

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The purpose of this laboratory study was to determine whether etching of flat bovine enamel surfaces with a 50 per cent aqueous solution of phosphoric acid for 60 seconds increases the bonding of a conventional restorative acrylic resin and a new polycarboxylate cement. The test specimens were subjected to 24 hours, 30 days and six months storage in water and then subjected to temperature stress cycling and intermittent tensile stress cycling. A tensile test was used to measure the bond strength of both materials.

The results of the Newman-Keul's test showed that pretreating the enamel surface with 50 per cent phosphoric acid significantly increased the bonding of the restorative resin, and that the cavity sealer supplied by the manufacturer further improved the resin attachment to enamel surfaces previously etched with phosphoric acid. The bonding of the resin to acid-etched enamel surfaces pretreated with or without the cavity sealer was unaffected by prolonged storage in water, temperature stress cycling, and

intermittent tensile stress cycling. However, a significant reduction in the adhesion of the acrylic resin to polished-enamel surfaces pretreated with or without the cavity sealer was observed when the test specimens were subjected to the same testing conditions.

The data obtained for the polycarboxylate cement test specimens showed that etching of the enamel surface with phosphoric acid also provided slightly higher adhesive values than the control specimens.

Results obtained revealed that prolonged storage in water, and temperature and mechanical stress cycling did not affect the adhesion of the polycarboxylate cement to acid-etched enamel surfaces. However, thermal and mechanical stress cycling after prolonged storage in water appeared to decrease the adhesion of the cement to polished enamel surfaces.

When Ca^{45} was used to assess the marginal seal of resin restorations placed into acid-etched Class V cavity preparations in extracted human teeth, the autoradiographs showed that etching of the cavity preparations with 50 per cent phosphoric acid improved the marginal seal of the restorative resin after one-week storage in water. When both the acid-etched and control restorations were thermal stress cycled 2500 times at a $40^{\circ}C$ temperature differential, a slight improvement in the marginal seal of the acid-etched restorations was observed.